

# OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT

## MODEL COVER SHEET

1. QA: QA

Page: 1 of 67

*Complete Only Applicable Items*

**2. Type of Mathematical Model**



Process Model



Abstraction Model



System Model

Describe Intended Use of Model:

To be used as input to License Application

Technical Contact/Department: Gopal De/Waste Package

**3. Title:**

Hydrogen Induced Cracking of Drip Shield

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ANL-EBS-MD-000006 REV 01

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# OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT

## MODEL REVISION RECORD

1. Page: 2 of 67

2. Model Title:

Hydrogen Induced Cracking of Drip Shield

3. DI (including Rev. No. and Change., if applicable):

ANL-EBS-MD-000006 REV 01

4. Revision/Change No.

5. Description of Revision/Change

00	Initial Issue
00/01	Interim Change Notice to include (1) hydrogen induced cracking due to the possible galvanic contact between the Ti-7 drip shield and steel components that may fall onto the drip shield in the case of a no-backfill drip shield design; and (2) approach to issue resolution status report key technical issue: container life and source term. Changes are indicated by vertical lines in the right margin.
00/02	Interim Change Notice to remove TBV-4897. Assumption 5.5 added, and Sections 6.3.3 and 8.1 modified. The input statuses of some of the references in the Document Input Reference System (DIRS) report have been revised. Changes made in this Analysis and Model Report are indicated by vertical lines in the right margin.
01	Document revised for Model Validation and NRC comment resolution. This extensive revision generated new sections 5.6, 6.1.6, 6.1.7, 6.2.5, 6.3.4, 6.3.5, 6.3.6, 7, and 10. The modified sections include 1.1, 1.2, 2, 3, 4.1, 4.2, 4.3, 5.3, 5.4, 5.5, 6.1.1, 6.1.5, 6.2.3, 6.2.4, 6.3.2, 6.3.3, 6.3.7, 8, and 9.

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## ACRONYMS AND ABBREVIATIONS

ACM	alternative conceptual model
AMR	Analyses and Model Report
HIC	hydrogen-induced cracking
LLNL	Lawrence Livermore National Laboratory
LTCTF	Long Term Corrosion Test Facility
PA	performance assessment
SAW	simulated acidic concentrated water
SCE	saturated calomel electrode
SCW	simulated concentrated water
SDW	simulated dilute water
SSW	simulated saturated water
TWP	Technical Work Plan

## 1. PURPOSE

### 1.1 PURPOSE AND BACKGROUND

One potential failure mechanism for titanium and its alloys under repository conditions is via the absorption of atomic hydrogen in the metal crystal lattice. The resulting decreased ductility and fracture toughness may lead to brittle mechanical fracture called hydrogen-induced cracking (HIC) or hydrogen embrittlement. For the current design of the engineered barrier without backfill, HIC may be a problem since the titanium drip shield can be galvanically coupled to rock bolts (or wire mesh), which may fall onto the drip shield, thereby creating conditions for hydrogen production by electrochemical reaction.

The purpose of this scientific analysis and modeling activity is to evaluate whether the drip shield will fail by HIC or not under repository conditions within 10,000 years of emplacement. This Analysis and Model Report (AMR) addresses features, events, and processes related to hydrogen induced cracking of the drip shield. REV 00 of this AMR served as a feed to *Waste Package Degradation Process Model Report* and was developed in accordance with the activity section "Hydrogen Induced Cracking of Drip Shield" of the development plan entitled *Analysis and Model Reports to Support Waste Package PMR* (CRWMS M&O 1999a). This AMR, prepared according to *Technical Work Plan for: Waste Package Materials Data Analyses and Modeling* (BSC 2002), is to feed the License Application.

Titanium Grade 7 (Ti-7) (UNS R52400) is now favored for construction of the drip shield for the waste package due to its excellent corrosion resistance (CRWMS M&O 2000a, Section 1.2). This alloy consists of 0.3% Fe, 0.25% O, 0.12-0.25% Pd, 0.1% C, 0.03% N, 0.015% H, 0.4% total residuals with the balance being Ti (CRWMS M&O 1999b, p. 45; DTN: MO9906RIB00052.000). Other titanium alloys that will be discussed in this report include Ti-2, Ti-5, Ti-12, Ti-16, Ti-17 and Ti-24. Ti-2 is essentially commercially pure titanium. It is believed that the most effective way of reducing hydrogen absorption is to choose a more crevice resistant alloy (Shoesmith et al. 1997, p. 15). This improvement in resistance to crevice corrosion can be attributed to the addition of alloying elements, which reinforce passivity. Therefore, susceptibility to crevice corrosion is reduced through the alloying series Ti-2→Ti-12→Ti-16 (Shoesmith et al. 1997, p. 15). The major additions are Ni (0.6-0.9%) for Ti-12 and Pd (0.04-0.08%) for Ti-16 (CRWMS M&O 1999b, pp. 49, 51; DTN: MO9906RIB00052.000). A decrease in the corrosion rate by the addition of a noble metal such as Pd in Ti-16 is noted in Shoesmith et al. (1997, p. 21). The composition of Ti-7 is almost identical to that of Ti-16, but the Pd content is higher in Ti-7 (0.12-0.25%) than in Ti-16 (0.04-0.08%) (CRWMS M&O 1999b, pp. 45, 51; DTN: MO9906RIB00052.000). The similarity between Ti-7 and Ti-16 was also noted by CRWMS M&O (2000a, Section 1.2).

The drip shield will experience a wide range of conditions during its service life (CRWMS M&O 2000a, Section 1.3). Initially, the underlying waste packages will be hot, and drip shield surfaces will be dry due to the heat generated from radioactive decay. The temperature will eventually drop to levels where both humid air and aqueous phase corrosion will be possible. Crevice corrosion and slow general passive corrosion will produce hydrogen, which can be absorbed into the metal. In a drip shield design without backfill, hydrogen generation may be caused by the

galvanic couple between the titanium drip shield surface and ground support components (such as rock bolts, wire mesh, and steel liners used in the drift), which may fall onto the drip shield surface.

HIC is a mechanism of premature failure of the drip shield, which is one of the most important principal factors, and should be considered in the repository performance assessment. In this AMR, a realistic model will be used to account for the degradation of the drip shield due to the effects of HIC induced by crevice corrosion and general corrosion, based upon data generated by the project. The model will follow the approach of Shoesmith et al. (1997). Both qualitative and quantitative assessments will be made to evaluate the effect due to the galvanic couple.

## **1.2 RESOLUTION OF COMMENTS IN THE NUCLEAR REGULATORY COMMISSION LETTER OF DECEMBER 21, 2001**

### **1.2.1 Resolution of Container Life and Source Term Agreement 6.02**

The NRC has requested the following information to support a potential licensing review (Reamer 2001, pp. 11-13):

1. Provide better justification and needs to verify that the critical hydrogen concentration chosen is a realistic and representative value for the onset of cracking in Ti Grade 7. An evaluation of the critical hydrogen concentration for Ti Grade 24 should also be given.

**Approach**—As mentioned in section 1.1, Ti-7 is similar to Ti-16 in terms of chemical composition; the only difference is that Ti-7 contains more palladium than Ti-16. In addition, Table 1 of Been and Grauman (2000) shows that the key mechanical properties of Ti-16 and Ti-7 are identical (minimum yield strength = 275 MPa; minimum tensile strength = 345 MPa). Since both of these alloys are  $\alpha$ -alloys containing minimal amounts of  $\beta$ -phase, it is expected that they will exhibit very similar responses to applied stresses in an acidic environment. Based on this argument, the value of  $H_C$  for Ti-7 would be expected to be at least that for Ti-16 (i.e.,  $\sim 1000 \mu\text{g/g}$ ).

A convincing argument can also be made that the rates of hydrogen absorption will be independent of the Pd content of the alloy. The rate of hydrogen absorption is influenced by many parameters including pH and temperature. The hydrogen absorption efficiency decreases dramatically with increasing pH (Foroulis 1980, Okada 1983; Phillips et al. 1974) and also with time at a constant pH (Noel et al. 1996, Figure 18). The results of Okada (1983) show a very significant drop in hydrogen absorption efficiency around pH 2. Over a 50-hour period Phillips et al. (1974) found no hydrogen absorption for pH = 10.3 and pH = 14. These measurements of hydrogen absorption (Okada 1983, Phillips et al. 1974) are based on accurate electrochemical measurements of hydrogen production rates and accurate measurements of the amount of hydrogen absorbed using the well-characterized vacuum degassing technique.

This influence of the presence of a surface oxide on the absorption efficiency is very marked. The results of Okada (1983) clearly suggest that any tendency for the Pd content in Ti to accelerate hydrogen absorption will be suppressed when a passive oxide is



present (i.e., for  $\text{pH} \geq 4$ ). It can be concluded that the primary factor controlling H absorption is the presence and properties of the passive oxide, not the noble metal content of the alloy. The results of Tomari et al. (1999) support this conclusion. The rate of hydrogen absorption was found to decrease parabolically with exposure time even under cathodically polarized conditions (equivalent to the presence of galvanic coupling with carbon steel) when hydrogen absorption would be expected to be accelerated through a reduced oxide film. The same parabolic relationship was obtained for Ti-2 and Ti-17 (equivalent to Ti-16 but with a slightly lower oxygen content). The observation of a parabolically decreasing rate is evidence that the absorption efficiency is decreasing with time. This suggests that surface absorption sites are becoming saturated and that the rate of absorption will eventually become controlled by the rate of diffusive transport within the titanium. For the  $\alpha$ -alloys (Ti-2, Ti-16, and Ti-7) this transport rate will be very low. The results of Kim and Oriani (1987a) show that a similar parabolic decrease in H absorption rate is observed on Ti-12, and the rate is almost independent of temperature in saturated brines close in composition to the most aggressive conditions expected in Yucca Mountain.

Further supporting evidence comes from observations made on Ti alloys covered by thermally grown oxides. The presence of such oxides have been shown to suppress hydrogen absorption in aggressive brine environments (6% NaCl) up to temperatures  $\sim 120^\circ\text{C}$  (Mon 2002, Attachment IV; Been and Grauman 2000; and Covington 1979), and the hydrogen absorption observed in deaerated HCl ( $2 \leq \text{pH} \leq 4$ ;  $50^\circ\text{C}$  to  $250^\circ\text{C}$ ) was completely stopped by aerated conditions (Shimogori et al. 1985).

The above mentioned evidence clearly suggests that the HIC behavior of Ti-7 should be at least as resilient as that of Ti-16.

The testing of Ti-5 and its Pd-modified version Ti-24 show that the addition of Pd to Ti-5 improves the alloy's corrosion resistance in an analogous manner to that observed when Pd is added to the Ti-2 alloy to produce Ti-16 (Schutz 1995; Schutz and Xiao 1993; and Kitayama et al. 1992). While the absolute corrosion performance of Ti-24 doesn't quite match that of Ti-16, it has many similar corrosion properties. The addition of Pd severely reduces the active corrosion rate in hot acidic solutions and eliminates susceptibility to crevice corrosion except in extremely aggressive conditions. Thus the alloy does not crevice corrode in naturally aerated 20% NaCl up to  $260^\circ\text{C}$ . The mechanism by which Pd improves the corrosion resistance is the same as in Ti-7 and Ti-16, i.e., the accumulation of Pd in the corroding surface ennobles the alloy. Also, hydrogen-charging studies (Kitayama et al. 1992) revealed no measurable influence of Pd addition to Ti-5 (to produce Ti-24) on the alloy's susceptibility to hydrogen absorption or embrittlement.

Although no specific measurements exist, there is no reason to expect that the general passive corrosion rates for Ti-24 will be significantly different from those observed for Ti-16, Ti-12, and Ti-7 in Long Term Corrosion Test Facility (LTCTF) measurements at Lawrence Livermore National Laboratory (LLNL). Ti-24 is an  $\alpha$ - $\beta$  alloy and, while the composition and physical structure of the passive oxide film will be slightly different on

this alloy compared to that on the  $\alpha$ -alloys (Ti-2, Ti-7, Ti-16) (Ask et al. 1988-89), this would not be expected to influence corrosion of the alloy under repository conditions. Any difference that might exist would only be expected under extreme conditions of acidity or alkalinity, especially in the former case if significant  $F^-$  concentrations were present in the exposure environment (Schutz and Thomas 1987). The mechanism by which  $F^-$  attacks Ti is through defects and/or flaws in the oxide. A greater probability of the existence of such flaws would be expected in the passive film on Ti-24 due to the differential oxide growth rates expected on the  $\alpha$ - and  $\beta$ -phases in the substrate. However, since Ti-24 will be located under the shell of the drip shield, it should not be exposed to the seepage drips, which could produce such conditions (i.e., differential oxide growth rates) by evaporative concentration.

As for the  $\alpha$ -alloys, whether or not the alloy is subject to HIC will be determined by the critical hydrogen concentration ( $H_C$ ) for slow crack growth and the rate of hydrogen absorption to achieve this critical concentration. The critical hydrogen concentration has been established for Ti-5 using similar experimental techniques employed to determine the critical hydrogen concentrations for Ti-2, Ti-12, and Ti-16 (Hardie and Ouyang 1999). Using the slow strain rate technique on precracked compact tension specimens precharged with known amounts of hydrogen, it was shown that the fracture toughness of Ti-5 was not significantly altered until the hydrogen level in the alloy exceeded 200  $\mu\text{g/g}$ . This compares to values of 400  $\mu\text{g/g}$  (Ti-2), 400  $\mu\text{g/g}$  (Ti-12) and  $\sim 1000$   $\mu\text{g/g}$  (Ti-16) (Shoesmith et al. 1997, 2000; Ikeda and Quinn 1998a). It seems likely that the presence of Pd will lead to a higher value of the critical hydrogen concentration in Ti-24 in a similar manner to the increase observed when adding the same amount of Pd to Ti-2 to produce Ti-16. In the absence of experimental measurements it is not possible to specify how much this improvement might be. A modest improvement to 400  $\mu\text{g/g}$  seems a reasonable  $H_C$  value for Ti-24.

A considerable amount of evidence exists to show that the rate of absorption of hydrogen is predominantly controlled by the properties of the oxide film, especially its thickness and defect properties (Pan et al. 1997; Blackwood et al. 1988; Hurlen and Hjornkol 1990). Since the alloy will experience a long period of slow thermal oxidation prior to exposure to aqueous conditions, it is the properties of this oxide that will determine the rate of hydrogen absorption. Thermally grown oxides on Ti-2 have been shown to suppress hydrogen absorption on subsequent exposure to aggressive brine solutions (up to 6% NaCl) up to temperatures  $\sim 120^\circ\text{C}$  (Mon 2002, Attachment IV; Been and Grauman 2000; and Covington 1979), and the hydrogen absorption observed in de-aerated HCl ( $2 \leq \text{pH} \leq 4$ ;  $50^\circ\text{C}$  to  $250^\circ\text{C}$ ) was completely stopped under aerated conditions (Shimogori et al. 1985). In the absence of exposure of the oxide film to seepage drips, Ti-24 would be expected to perform just as well.

2. Provide an evaluation of possible detrimental effects of fluoride on hydrogen uptake and its effects on the critical hydrogen concentration and subsequent cracking.

**Approach**—Detailed description of the detrimental effects of fluoride on titanium has been provided in Section 1.2.2. As mentioned therein, the influence of fluoride on

hydrogen absorption by titanium is expected to be proportional to the active corrosion rate and the period for which it can sustain it. The primary damage mode for titanium under these circumstances will be the loss of wall thickness due to titanium dissolution (via complex formation with  $F^-$ ), not the increase in hydrogen content of the alloy leading to early failure by HIC.

Again, as explained in Section 1.2.2, under repository conditions at Yucca Mountain, the Ti-7 drip shield surface will be covered with an oxide grown relatively slowly under thermal conditions. Such a film is expected to have a low defect density (Pan et al. 1997; Blackwood et al. 1988) and, hence, should be highly resistant to dissolution including that induced by reaction with  $F^-$ . Moreover, the repository environment at Yucca Mountain contains lots of silica along with a variety of metal ions, which have the potential to consume  $F^-$  ions, and thereby reduce the deleterious effects of fluoride on the Ti-7 drip shield to a very low level. Support of this view is provided by the observation that, during evaporation of J-13 water, the concentration of  $F^-$  continued to decrease (due to precipitation) and ultimately dropped below the level of detection (CRWMS M&O 2000a, Section 4.1.2).

Finally, it is to be noted that  $H_C$  is a material property and, hence, it should not be affected by an increase in corrosion rate of the material concerned (i.e., Ti-7) in the presence of  $F^-$  ions. Most probably, this is why the effect of fluoride on  $H_C$  for Ti-7 has not received attention in the past, and it is for this reason that a recent literature search did not find a published scientific article focused on this topic.

3. Provide the results for the Ti Grade 24 structural drip shield components.

**Approach**—See approach for item number 1 mentioned above.

### 1.2.2 Resolution of Container Life and Source Term Agreement 6.03

The NRC has requested the following information to support a potential licensing review (Reamer 2001, pp. 11-13):

Provide an evaluation of the possible detrimental effects of fluoride on possible hydrogen uptake rates, as well as enhanced corrosion resulting in higher than currently estimated hydrogen generation rates.

**Approach**—Fluoride is reported to be corrosive to titanium and its alloys over the full range of concentrations (Schutz and Thomas 1987). In general, the susceptibility of titanium to corrosion in environments containing  $F^-$  is attributed to the formation of complex anions, such as  $TiF_6^{2-}$  and  $TiF_6^{3-}$ , which are highly stable and soluble in electrolyte solutions (Reclaru and Meyer 1998; Brossia and Cragolino 2001). A few previous reports have noted that, in the absence of fluoride inhibitors (e.g.,  $Al^{3+}$ ,  $Fe^{3+}$ , etc.), solutions containing over 20 ppm of  $F^-$  may attack titanium when the solution pH drops below 6–7 (Schutz and Thomas 1987; Pulvirenti et al. 2002). However, measurements of corrosion potential by a number of other researchers suggest that a combination of a significant  $F^-$  concentration ( $> 500 \mu g/g$ ) and a low pH is critical for the loss of passivity of titanium

alloys (Nakagawa et al. 1999; Nakagawa et al. 2001; Reclaru and Meyer 1998; Lorenzo de Mele and Cortizo 2000; Wilhelmsen and Grande 1987). In artificial saliva (at 37°C) passivity was maintained in solutions containing 500–1000 ppm F<sup>-</sup> providing the pH was above 4.3. For lower pH values the corrosion potential fell from the range 0 to -500 mV (vs. saturated calomel electrode [SCE]) to -850 mV. The latter potentials are a clear indication that aggressive active corrosion conditions had been established. Analyses of Ti concentrations in solution, using Inductively Coupled Plasma Emission Spectroscopy-Mass Spectrometry, confirmed this loss of passivity (Nakagawa et al. 1999). Polarization curves confirmed the introduction of an active region and also a significant increase in passive current densities at more positive potentials (Nakagawa et al. 2001). Thus, the passive current density in the presence of 500 ppm F<sup>-</sup> increased as follows; 10  $\mu\text{A}/\text{cm}^2$  (pH = 5), 20–30  $\mu\text{A}/\text{cm}^2$  (pH = 4.5), 40–50  $\mu\text{A}/\text{cm}^2$  (pH = 4.3), 60–90  $\mu\text{A}/\text{cm}^2$  (pH = 4.2), 400  $\mu\text{A}/\text{cm}^2$  (pH = 4.0), and 700  $\mu\text{A}/\text{cm}^2$  (pH = 3.0) (Nakagawa et al. 2001). It should be noted that while these values illustrate the dependence on pH the absolute values should be treated with caution since they were recorded under dynamic polarization conditions and the films are not representative of steady-state defect-annealed oxide films.

The importance of the condition of the passive film was demonstrated by Lorenzo de Mele and Cortizo (2000). Their measurements, conducted in synthetic saliva (pH = 6.5) containing 0.2 mol/L of F<sup>-</sup>, showed that if the F<sup>-</sup> was added shortly after electrode immersion while the oxide film was still growing, then the corrosion potential fell rapidly indicating attack of the oxide. However, if the oxide was allowed to grow for 4 days, a sufficient period for the annealing out of most of the defects in the oxide, then the subsequent addition of this concentration of F<sup>-</sup> had no observable effect over the subsequent 2 days of exposure. They concluded that the susceptibility to F<sup>-</sup> was associated with defects and flaws in the oxide.

These results (Lorenzo de Mele and Cortizo 2000) strongly suggest that the influence of F<sup>-</sup> is via the same mechanism as that involved for Cl<sup>-</sup> and requires that F<sup>-</sup> utilize defects within the oxide in order to initiate oxide breakdown rather than chemically-attacking the outer oxide surface. Polarization curves recorded by Lorenzo de Mele and Cortizo (2000) at different [F<sup>-</sup>] showed that a conventional breakdown potential could be observed. This breakdown potential decreased from +0.4 V (vs. SCE) in 0.02 mol/L NaF to -0.25V for 0.5 mol/L NaF. The presence of blisters in the oxide film after polarization experiments (observed by Scanning Electron Microscopy) confirmed the local, as opposed to general, attack of the oxide in the presence of F<sup>-</sup>.

Pan et al. (1997) showed that the oxide defect density, determined from film capacitance measurements using Mott–Schottky plots, for films produced by ion-beam assisted sputtering deposition had both a lower defect density and a lower passive current density than those of oxides grown under natural corrosion conditions in aqueous solutions. These results clearly connect the passive dissolution rate to the density of defects in the oxide and are consistent with the results of Blackwood et al. (1988) who also found a rate of dissolution dependent on defect density (e.g., degree of crystallinity) of the oxide film and with the claims of Hurlen and Hjornkol (1990) that the kinetics of passive corrosion of

titanium in neutral solutions is controlled by the migration of the predominant defect, an oxygen vacancy across the oxide film.

In the presence of fluoride, the rate of hydrogen absorption would be expected to be proportional to the rate of the corrosion process, as it would be under active corrosion conditions within a crevice (Noel et al. 2001). Even under these conditions there is accurate electrochemical evidence to show that the hydrogen absorption efficiency decreases with time (Noel et al. 1996). This can be attributed to the formation of a surface hydride layer leading to control of the hydrogen absorption process by transport across this layer. This conclusion is consistent with the extensive results of Phillips et al. (1974). Once this layer is formed, its removal by anodic dissolution and reformation by the cathodic reduction of protons achieve steady state and the rate of hydrogen absorption becomes controlled by the rate of diffusion of hydrogen into the alloy from the hydride/alloy interface (Shoesmith et al. 2000).

Thus, the influence of fluoride on hydrogen absorption will be proportional to the active corrosion rate it can sustain and the period for which it can sustain it. The primary damage mode under these circumstances will be the loss of wall thickness, not the increase in hydrogen content of the alloy leading to early failure by HIC.

A number of species, in particular certain compounds containing elements from groups V and VI of the periodic table (e.g., oxyanions of S, Sb, Se, Te, and CN<sup>-</sup>), are known to be catalysts for hydrogen absorption (Jones 1996, p. 335). These promoters act by retarding the formation of molecular hydrogen gas and enhancing the residence time of hydrogen atoms on the surface, thereby facilitating its absorption into the metal. A specific interaction with surface-adsorbed H-states is required for a chemical species to act as a catalyst to increase the hydrogen absorption efficiency. There is no evidence that halide ions can interfere with the hydrogen absorption process in this manner. Consequently, fluoride is not expected to function as a catalyst for hydrogen absorption.

Finally, based on the above discussion it can be concluded that F<sup>-</sup> attack of passive titanium requires acidic conditions (pH ~ 4) as well as the presence of flaws in the oxide which allow access of F<sup>-</sup> to the metal surface and the establishment of localized acidic conditions. Once these conditions are established, attack of the metal by F<sup>-</sup> is rapid. This raises a question as to why Brossia and Cragnolino (2001) observed aggressive active corrosion of Ti in neutral 1 mol/L NaCl solution. Two factors appear to be important in understanding their work:

1. The values were recorded in polarization experiments on freshly prepared Ti specimens covered only with a defective anodic film. As discussed above, attack of the metal by F<sup>-</sup> is to be expected on such surfaces.
2. The temperature was 95°C, a value at which flaws could develop in the solution-grown oxide film on Ti (Shibata and Zhu 1995).

By contrast, under repository conditions at Yucca Mountain, the Ti-7 drip shield surface will be covered with an oxide grown relatively slowly under thermal conditions, and

scientific evidence exists (see Section 1.2.1) to show such a film will have a low defect density and, hence, should be highly resistant to dissolution including that induced by reaction with  $F^-$ . Moreover, the repository environment at Yucca Mountain contains silica and a variety of metal ions, which have the potential to consume  $F^-$  ions, and thereby keep the deleterious effects of fluoride on the Ti-7 drip shield at a very low level. This view is supported by the observation that, during evaporation of J-13 water, the concentration of  $F^-$  decreased (due to precipitation) and ultimately dropped below the level of detection (CRWMS M&O 2000a, Section 4.1.2).

## **2. QUALITY ASSURANCE**

The Office of Civilian Radioactive Waste Management Quality Assurance program applies to this AMR. All types of waste packages were classified per QAP-2-3 as Quality Level-1. CRWMS M&O (1999c, p. 7), *Classification of the MGR Uncanistered Spent Nuclear Fuel Disposal Container System*, is cited as an example of a waste package type. This classification is still in effect. The applicability of *Quality Assurance Requirements and Description* requirements (DOE 2002) to Revision 00, ICN 01, and ICN 02 activities was established in activity evaluation, *1101213PM7 Waste Package Analysis & Models - PMR* (CRWMS M&O 1999d), which was prepared per QAP-2-0. These earlier versions of this AMR were developed in accordance with the development plan (CRWMS M&O 1999a) and AP-3.10Q, *Analyses and Models*. Consistent with this development plan, no special controls on the electronic management of data were necessary in these activities.

This revision of the AMR has been developed per AP-SIII.10Q procedure under *Technical Work Plan for: Waste Package Materials Data Analyses and Modeling* (BSC 2002), which, in turn, was developed in accordance with AP-2.27Q, *Planning for Science Activities*. The applicability of *Quality Assurance Requirements and Description* requirements (DOE 2002) is documented in the technical work plan (TWP) (BSC 2002, Section 8). A process control evaluation was performed in accordance with AP-SV.1Q, *Control of the Electronic Management of Information*. Results documented in Addendum A of the technical work plan (BSC 2002) specifies measures to be adopted for the electronic management of data/information.

## **3. USE OF SOFTWARE**

No computer software or models have been used to support the development of the analysis and modeling activities described in this AMR.

## 4. INPUTS

### 4.1 DATA AND PARAMETERS

The following input data and/or parameters are obtained from Weast (1978, p. B-177):

$\rho_{Ti}$  = density of titanium

$M_{Ti}$  = Molecular weight of titanium

The following input data and/or parameters for Ti-7 are obtained from CRWMS M&O (2000a, Section 6.5.4):

$R_{uc}$  = passive general corrosion rate (maximum).

The following design parameters are obtained from BSC (2003) and 10 CFR 63.114(d), respectively:

$d_0$  = Half of drip shield thickness

$t$  = time of emplacement

For project consistency, these parameters have been tabulated as shown in Table 1. All of these input data and parameters contained in Table 1 will be used to evaluate the HIC effects on the drip shield.

Table 1. Input Parameters

Parameter Name	Parameter Source	DTN	Parameter Value(s)	Units	Distribution (or single value if fixed)
$\rho_{Ti}$ = Density of titanium	Weast 1978, p. B-177	N/A	4.5	g/cm <sup>3</sup>	Fixed value
$M_{Ti}$ = Molecular weight of titanium	Weast 1978, p. B-177	N/A	47.9	N/A	Fixed value
$R_{uc}$ = Rate of general passive corrosion (maximum)	N/A	DTNs: MO0003SPASUP02.003 LL990610605924.079	$3.88 \times 10^{-4}$ $1.76 \times 10^{-4}$	mm/year mm/year	Maximum value Maximum value
$d_0$ = Half of drip shield thickness	BSC 2003	N/A	7.5	mm	Fixed value
$t$ = time of emplacement	10 CFR 63.114(d)	N/A	10,000	years	Fixed value

In general, for the input parameters of the HIC Model, a conservative approach will be used in that input values at (or near) lower or upper bounds (as appropriate) will be used to ascertain that

the estimated output value is conservative. However, the primary sources of uncertainty in the HIC Model are associated with the selection of values for the rate of general passive corrosion,  $R_{uc}$ , and the fractional hydrogen absorption efficiency,  $f_h$ , discussed in Section 5.5. In evaluating the model, the maximum values for these parameters will be used for a conservative estimate of hydrogen concentration in the drip shield.

For the purposes of this analysis, the maximum possible general corrosion rate of the drip shield is considered to be  $3.88 \times 10^{-4}$  mm/year (DTN: MO0003SPASUP02.003). This value results from measurements of the corrosion rate of samples with both weight-loss and creviced geometries (and corrected for potential effects of silica deposition). Conceptually, this general corrosion rate would be appropriate for use only on the drip shield outer surface since only the drip shield outer surface could be contacted by dripping water. Dripping water could potentially lead to the formation of scale and/or salt deposits under which crevice conditions could form. On the underside of the drip shield, no crevice conditions are possible as only condensed (hence relatively impurity-free) water could contact these regions. Therefore, the maximum possible general corrosion rate for the underside of the drip shield is considered to be  $1.76 \times 10^{-4}$  mm/year (DTN: LL990610605924.079). This value results from measurements of the corrosion rate of samples with weight-loss geometries only (and corrected for potential effects of silica deposition). Since the rate of hydrogen generation on the drip shield surface, and hence the rate of hydrogen absorption into the drip shield, will be proportional to the rate of drip shield corrosion, and the two surfaces of the drip shield are to corrode at two different rates, the average of these two maximum corrosion rates,  $2.82 \times 10^{-4}$  mm/year, is appropriate for its use in the HIC model.

## 4.2 CRITERIA

The Waste Package Technical Work Plan (BSC 2002, Table C5) has identified the following acceptance criteria (AC) from *Project Requirements Document* (Curry and Loros 2002) and *Yucca Mountain Review Plan, Draft Report for Comment* (NRC 2002). According to the Waste Package TWP (BSC 2002, Section 3), this AMR is to address only these applicable acceptance criteria:

1. System Description and Demonstration of Multiple Barriers (Curry and Loros 2002, PRD-002/T-014, PRD-002/T-016; NRC 2002, Section 4.2.1.1.3)
  - AC1: Identification of barriers is adequate.
  - AC2: Description of the capability of identified barriers is acceptable.
2. Degradation of Engineered Barriers (Curry and Loros 2002, PRD-002/T-015; NRC 2002, Section 4.2.1.3.1.3)
  - AC1: System description and model integration are adequate.
  - AC2: Data are sufficient for model justification.



### 4.3 CODES AND STANDARDS

The acceptance criteria listed in Section 4.2 are consistent with the methodology described in the ASTM Standard Practice C 1174 for prediction of the long-term behavior of engineered barrier system components in a geologic repository (ASTM C 1174-97 1998).

## 5. ASSUMPTIONS

The following assumptions are used for the HIC model of this AMR. The technical basis for each assumption is also provided so that these assumptions require no further verification.

- 5.1 Due to the close similarity in chemical composition between Ti-7 and Ti-16, available material property data for Ti-16 are assumed to be applicable to Ti-7 if the said material property data are not available for Ti-7. This assumption is used in Sections 5.2, 6.1, and 6.2.
- 5.2 The  $H_C$  value for Ti-7 is assumed to be at least 1000  $\mu\text{g/g}$ . This assumption is based on Assumption 5.1 and results reported by Ikeda and Quinn (1998a, p. 7), which indicated that the  $H_C$  value for Ti-16 is between 1000 and 2000  $\mu\text{g/g}$ . This assumption is necessary because  $H_C$  data are not available for Ti-7. This value is conservative on a number of counts: (1) the value of 400  $\mu\text{g/g}$  is the lower limit of the measured range of 400 to 1000  $\mu\text{g/g}$  measured at room temperature ( $\sim 25^\circ\text{C}$ ) for Ti-2 (Shoesmith et al. 1997, pp. 7-11); (2) the temperature of the drip shield will be well above room temperature for the majority of its anticipated lifetime and Clarke et al. (1995) have shown  $H_C$  for both Ti-2 and Ti-12 rises to  $\sim 1000\mu\text{g/g}$  at a temperature of  $92^\circ\text{C}$  to  $100^\circ\text{C}$ ; and (3) the value of 400  $\mu\text{g/g}$  was measured for Ti-2, whereas the value for Ti-16, a palladium containing  $\alpha$ -alloy with similar properties to Ti-7, appears to be  $> 1000 \mu\text{g/g}$  (Ikeda and Quinn 1998a, p.7). This assumption is used in Sections 6.1.3 and 6.2.2.

It is noted that 400  $\mu\text{g/g}$ , the lower bound value observed for other titanium alloys (e.g., Ti-2 and Ti-12) by Shoesmith et al. (1997, pp. 7-11), was used as the critical hydrogen concentration for Ti-7 in REV 00 of this AMR. As discussed above, this value appears to be very conservative based on data reported by Ikeda and Quinn (1998a, p. 7).

- 5.3 Mechanisms for hydrogen generation and absorption on a titanium surface may include a galvanic couple, hydrogen produced in atomic form by the corrosion process, and the direct absorption of hydrogen produced by water radiolysis. As indicated by Shoesmith et al. (1997, p. 17), the direct absorption of radiolytically produced hydrogen is insignificant except at high dose rate ( $> 10^2 \text{ Gy/h}$ ) and high temperature ( $> 150^\circ\text{C}$ ), clearly unattainable under Yucca Mountain drip shield conditions. Therefore, only generation and absorption of hydrogen produced by general passive corrosion and by corrosion in the presence of a galvanic couple are considered in this AMR.
- 5.4 The passive oxide film growth rate and, hence, the corrosion rate are assumed to be constant in time for the formula used to calculate the concentration of hydrogen in the metal (Shoesmith et al. 1997, p. 22). The rationale for this assumption is that the assumption of constant corrosion rate is conservative, and less conservative corrosion

models assume that the rate decays with time (CRWMS M&O 2000a, Section 5.3). It is also implicit in this assumption and this formula that any hydrogen absorbed into the titanium remains within the remaining wall thickness and is not subsequently removed as the general corrosion process progresses with time. This is a very conservative assumption, since any titanium hydride formed within the alloy will be unstable with respect to titanium oxide (Beck 1973) and should, therefore, be removed by the general corrosion process. This assumption is used in Sections 6.1.5, 6.1.6, and 6.2.3.

- 5.5 High and low values for fractional efficiency of hydrogen absorption,  $f_h$ , for titanium alloys have been assumed to be 0.015 and 0.005, respectively. The rationale for this assumption is that these values were adopted from the results of experimental measurements by Okada (1983) performed under extremely conservative environmental conditions. These aggressive electrochemically polarized conditions are considered unachievable in the proposed repository at Yucca Mountain. For example, they were measured on Ti-2 under constant applied current conditions with an applied current of  $0.5 \text{ mA/cm}^2$  in acidic sodium sulfate solutions of  $\text{pH} = 4$  (at  $25^\circ\text{C}$ ). Under these conditions, the electrode potential achieved is  $< -1.0\text{V}$  (vs. SCE), 250 to 400 mV more negative than would be anticipated under even galvanic coupling conditions to carbon steel (Hodgkeiss et al. 1987). At these potentials redox transformations in the oxide will render it permeable to hydrogen (Shoesmith et al. 1997, Figure 2 and p. 2). However, this permeability will not be present under non-galvanic conditions. Furthermore, the impermeability of the passive oxide has been shown to be improved by thermal oxidation prior to immersion (Mon 2002, Attachment III). Such conditions are expected to prevail for an extensive period of emplacement in the repository prior to wetting.

Although  $f_h$  decreases with time as noted by Noel et al. (1996, Figure 18) and Tomari et al. (1999, Table 1), a value of 0.015 has been conservatively assumed constant throughout 10,000 years. This value is exceedingly conservative in comparison with the  $f_h$  value of 0.00014 reported by Tomari et al. (1999, Table 1) on the basis of experiments conducted for 1,440 hours under electrochemically polarized conditions. This conservative assumption has been used in Sections 6.1.5, 6.1.6, 6.2.3, 6.3.3, and 6.3.5.

- 5.6 The extent of galvanic corrosion due to coupling between carbon steel and Ti-7 will be limited by the small area of wet contact between these two metals, and the low cathode-to-anode ratio (Ti/Fe) which is likely to approach one. This is a rational assumption because the point of galvanic contact also simultaneously experiencing seepage drips is likely to be an incident of very low probability. The resulting inability of the site to remain wet due to run-off and the accumulation of iron oxide corrosion products will significantly impede galvanic corrosion. The passivating effects of iron oxides on the Ti surface and the presence of ferric ions in the corrosive solutions are well known in the scientific literature (Covington and Schutz 1981; Schutz and Thomas 1987). In view of these limitations, the mass of steel that could be consumed by galvanic corrosion and the initial contact area are assumed to be 22.727 kg (50 lbs) and  $75 \text{ cm}^2$ , respectively. These assumptions have been used in Section 6.3.4 and 6.3.5.

5.7 A mathematical model and an alternative conceptual model (ACM) are proposed in Sections 6.3.3 and 6.3.5, respectively, to predict the hydrogen concentration in the drip shield due to a galvanic coupling between the drip shield and a carbon steel segment. Simplifying assumptions are employed to develop the mathematical model. Because the assumptions are to simplify the system for the mathematical model, they do not require a technical basis or verification. These assumptions are:

- The drip shield is treated as an infinite flat plate. This is a conservative assumption since it allows a larger surface area to be available for galvanic coupling between the drip shield and a carbon steel segment than would be the case with a curved drip shield structure. This assumption is also to simplify the geometry for the mathematical model.
- The wetted contact plane between the drip shield surface and the carbon steel segment is circular in shape. This assumption is also to simplify the geometry for the mathematical model.
- Hydrogen is absorbed into the drip shield through the wetted contact plane and immediately reaches the other surface. The initial region of the drip shield experiencing hydrogen absorption has the shape of a circular disk. This assumption is also to simplify the geometry for the mathematical model.
- As hydrogen starts to diffuse in the drip shield, the radius of the circular region containing hydrogen will expand at a constant speed. This assumption is also to simplify the geometry for the mathematical model.

## **6. ANALYSIS/MODEL**

### **6.1 DESCRIPTION OF MODEL FOR HYDROGEN INDUCED CRACKING**

#### **6.1.1 Introduction**

The purpose of this scientific analysis and modeling activity is to evaluate whether the drip shield will fail by HIC or not under repository conditions within 10,000 years of emplacement. This AMR addresses features, events, and processes related to hydrogen induced cracking of the drip shield.

The drip shield will experience a wide range of conditions during its expected service life of 10,000 years (CRWMS M&O 2000a, Section 1.3). Initially, the underlying waste packages will be relatively hot, and drip shield surfaces will be dry due to the heat generated from radioactive decay. The temperature will eventually drop to levels where both humid air and aqueous phase corrosion will be possible. Crevice corrosion and slow general passive corrosion may be initiated and propagate in the metal. Both types of corrosion will produce hydrogen, which can be absorbed into the metal (Shoesmith et al. 1997, p. 2). In a drip shield design without backfill, hydrogen generation may be caused by the galvanic couple between the titanium drip shield surface and the ground support (such as rock bolts, wire mesh, and steel liners used in the drift), which may fall onto the drip shield surface.

Failure occurs if (1) the wall penetration by corrosion exceeds the corrosion allowance or if (2) the amount of hydrogen absorbed exceeds the critical hydrogen concentration,  $H_C$ , for failure due to hydrogen induced cracking (Clarke et al. 1994, Figure 8). The first type of failure mechanism, i.e., wall penetration by crevice and general corrosion, is treated in another AMR (CRWMS M&O 2000a). This AMR deals with the failure mechanism associated with HIC.

HIC (also called hydrogen embrittlement) is characterized by decreased fracture toughness or ductility of the metal due to absorbed atomic hydrogen. The usual mechanical failure mode for a ductile material is the ductile tearing observed during slow crack growth. Decreased fracture toughness causes fast crack growth (brittle fracture) of a normally ductile material under sustained load. During slow crack growth, the material will fail as the stress intensity factor  $K$  reaches a value  $K_S$ . During fast crack growth, the same material will fail as the stress intensity factor  $K$  reaches a value  $K_H$ , which is less than  $K_S$  (Shoesmith et al. 1997). Figure 1 (Shoesmith et al. 1997, page 9, Figure 7) represents, schematically, the combinations of stress intensity factor and hydrogen concentration leading to (1) fast crack growth (brittle fracture) controlled by  $K_H$ , (2) slow crack growth controlled by  $K_S$  due to either sustained load cracking or ductile rupture, or (3) no failure.

For corrosion induced HIC, an approach has been adopted to predict when HIC might become a potential failure process for the drip shield, following a Canadian precedent (Shoesmith et al. 1997). The basic premise of the model is that failure will occur once the hydrogen content exceeds a certain limit or critical value. Both qualitative and quantitative assessments will be conducted to evaluate the effect due to the galvanic coupling.

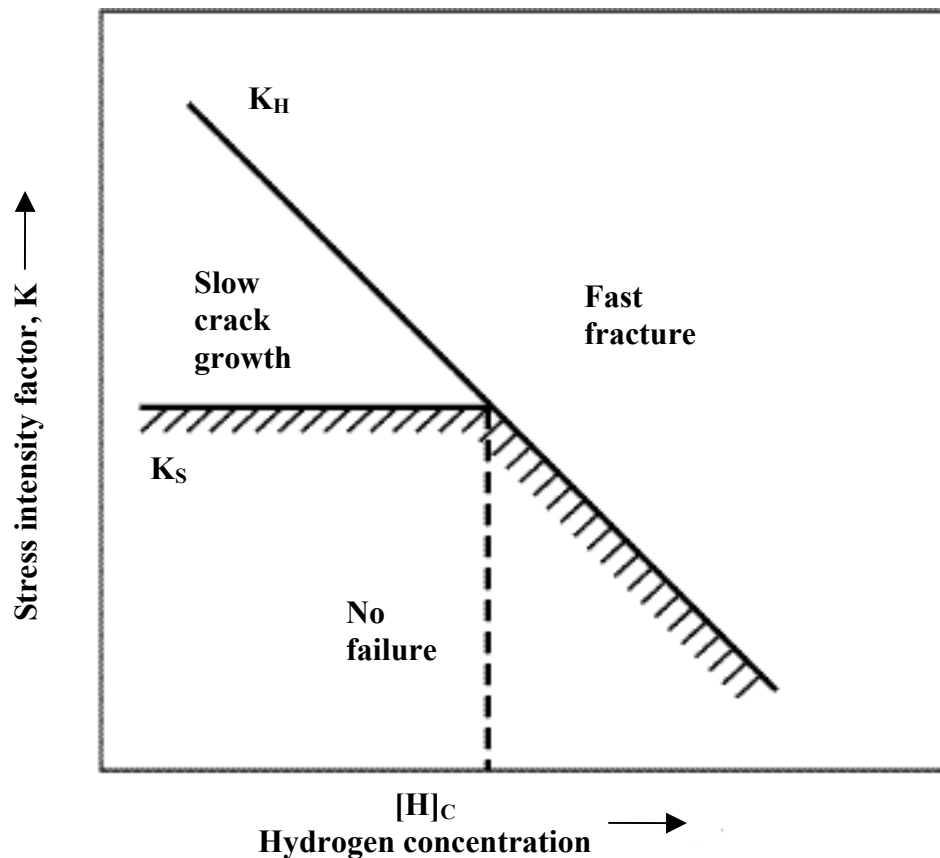
This report will address:

- Processes by which Ti-7 can absorb hydrogen and, hence, eventually become susceptible to HIC

- Analysis procedures for predicting the consequences of hydrogen absorption

- Acquisition of input data for the analysis parameters

- Results.



SL\_AMR1\_fig6

Source: Shoesmith et al. 1997.

Figure 1. Schematic Showing the Combinations of Stress Intensity Factor and Hydrogen Concentration Leading either to Fast Crack Growth (Brittle Failures) or Slow Crack Growth due to either Sustained Load Cracking or Ductile Rupture or to No Failure

### 6.1.2 Processes by which Hydrogen is Absorbed

In accordance with Schutz and Thomas (1987, p. 673), factors have been identified that can lead to HIC, i.e., hydrogen uptake and possible embrittlement of  $\alpha$  and near- $\alpha$  titanium alloys (such as titanium grade 2, grade 7 and grade 12) in aqueous media. The three general conditions that must exist simultaneously for the hydrogen embrittlement of  $\alpha$  alloys are:

A mechanism for generating hydrogen on a titanium surface. The mechanisms may include a galvanic couple, hydrogen produced in atomic form by the corrosion process, and the direct absorption of hydrogen produced by water radiolysis. As indicated in Section 5 (Assumption 5.3), the direct absorption of radiolytically produced hydrogen is insignificant except at high dose rate ( $> 10^2$  Gy/h) and high temperature ( $> 150^\circ\text{C}$ ), clearly unattainable under Yucca Mountain drip shield conditions. Therefore, only hydrogen produced by a galvanic couple and by general corrosion are considered in this AMR.

A metal temperature above approximately  $80^\circ\text{C}$  ( $175^\circ\text{F}$ ) when the diffusion rate of hydrogen into  $\alpha$  titanium becomes significant.

A solution pH less than 3 or greater than 12 or impressed potentials more negative than -0.7 V (SCE).

Assessment of HIC due to the effects of a galvanic couple will be presented in Section 6.3. The remainder of Section 6.1 and Section 6.2 will be devoted to HIC resulting from hydrogen produced by corrosion of titanium.

Both crevice corrosion and general passive corrosion will be accompanied by hydrogen production and, hence, possibly by the absorption of hydrogen into the metal.

For crevice corrosion the hydrolysis of dissolved metal cations leads to acidification within the occluded area and the development of active conditions in which the metal is unprotected by an oxide film. Once initiated, crevice corrosion is supported by both the reduction of oxygen on passive surfaces external to the crevice and the reduction of protons ( $\text{Ti} + 4\text{H}^+ \rightarrow \text{Ti}^{4+} + 2\text{H}_2$ ) on exposed metal surfaces inside the crevice. The latter process can lead to the absorption of atomic hydrogen into the metal in sufficient quantities to produce extensive hydride formation (Shoesmith et al. 1997, Figure 3, p. 4).

For the passive non-creviced or inert crevice conditions expected to prevail, the corrosion of the titanium alloy will be sustained by reaction with water under neutral conditions ( $\text{Ti} + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 2\text{H}_2$ ) and will proceed at an extremely slow rate. This process will generate hydrogen, which must pass through the  $\text{TiO}_2$  film before absorption into the underlying Ti alloy can produce HIC. Redox transformations ( $\text{Ti}^{\text{IV}} \rightarrow \text{Ti}^{\text{III}}$ ) in the film are required before the oxide becomes significantly transparent to hydrogen. Significant cathodic polarization of the metal (generally only achievable by galvanic coupling to carbon steel or the application of a cathodic protection potential) is required for these transformations to occur. Measurements of absorbed hydrogen suggest a threshold potential of -0.6 V versus SCE above which no absorption occurs (Shoesmith et al. 1997, p. 4). Only impressed current cathodic protection or galvanic coupling to active alloys such as Fe, Zn, or Mg could produce such cathodic potentials. Thus, hydrogen generation rates, and, hence, hydrogen absorption rates, are expected to be very low on Ti alloy surfaces.

### 6.1.3 Critical Hydrogen Concentration, $H_C$

Provided that wall penetration by corrosion does not exceed the corrosion allowance, HIC failure is assumed to occur when the material has absorbed enough hydrogen to exceed the critical hydrogen content,  $H_C$ . Observations regarding the critical hydrogen content,  $H_C$ , for Ti-2 and Ti-12 are summarized as follows:

Using the slow strain rate technique on precracked compact tension specimens precharged with known amounts of hydrogen, it has been shown that the fracture toughness of Ti-2 and Ti-12 is not significantly affected until the hydrogen content exceeds  $H_C$ . Once above  $H_C$ , there is no slow crack growth, and only fast crack growth is observed.

$H_C$  is sensitive to the microstructure and texture of the material with respect to the orientation of the crack and the applied stress. Preferential pathways for cracking are formed along  $\beta$ -phase stringers introduced through the manufacturing process. An  $H_C$  of 500  $\mu\text{g/g}$  has been measured

in Ti-12 containing cracks propagating in the directions defined by these stringers. Crack propagation perpendicular to these features is not observed up to  $H_C = 2000 \mu\text{g/g}$ . Heat treatment to remove this laminar structure by randomly reorienting the residual  $\beta$ -phase can lead to a decrease in  $H_C$  to  $\sim 400 \mu\text{g/g}$ .

Even for manufactured plate materials that do not have high  $\beta$ -phase content, e.g., Ti-2, the laminar structure introduced by rolling appears to dominate the cracking behavior. As a consequence, depending on crack orientation,  $H_C$  varies between  $\sim 400$  and  $1000 \mu\text{g/g}$ . Since Ti-2 does not contain as much  $\beta$ -phase as Ti-12, heat treatment does not exert a significant influence on  $H_C$ . Welding produces a larger change in the microstructure than does heat treatment. The high weld temperature results in significant microstructural changes in the weldment. This results in a small decrease in strength. The heat affected zone does not appear to be sufficiently large to influence the cracking behavior because, for both Ti-2 and Ti-12,  $H_C$  is slightly decreased near the weld metal compared to the base metal. It did not decrease below  $500 \mu\text{g/g}$ .

It can also be assumed that failure is less likely at elevated temperature. This assumption is justified, in part, by recognizing that the hydrogen solubility would be higher at elevated temperature. However, it has also been shown experimentally that  $H_C$  increases markedly with temperature (Clarke et al. 1995). While the maximum critical stress intensity factor for Ti-2 decreases slightly from  $\sim 50 \text{ MPa}\cdot\text{m}^{1/2}$  to  $\sim 40 \text{ MPa}\cdot\text{m}^{1/2}$  at  $95^\circ\text{C}$ , only slow crack growth was observed up to hydrogen concentrations of  $\sim 2000 \mu\text{g/g}$ , clearly indicating an enhanced resistance to growth of brittle-like cracks as the temperature is increased. A similar increase in resistance to brittle fracture was observed for Ti-12 at  $95^\circ\text{C}$ , the maximum stress intensity factor decreasing from  $\sim 60 \text{ MPa}\cdot\text{m}^{1/2}$  to  $\sim 45 \text{ MPa}\cdot\text{m}^{1/2}$ , while  $H_C$  increased to  $\sim 1000 \mu\text{g/g}$  (Clarke et al. 1995). Preliminary creep measurements clearly indicate that increased creep deformation at higher temperatures was a major factor in preventing the development of a sufficiently high stress concentration to initiate fast fracture (Clarke et al. 1995).

$H_C$  data are not available for Ti-7 but more recent data reported by Ikeda and Quinn (1998a, p. 7) indicated that the  $H_C$  value for Ti-16 is between  $1000$  and  $2000 \mu\text{g/g}$ . As noted in Section 1, Ti-7 and Ti-16 are similar alloys because of their similar chemical compositions.

The  $H_C$  value for Ti-7 is assumed to be at least  $1000 \mu\text{g/g}$ . This assumption is based on Assumption 5.1 and data reported by Ikeda and Quinn (1998a, p. 7), which, as indicated earlier, concluded that the  $H_C$  value for Ti-16 is between  $1000$  and  $2000 \mu\text{g/g}$ . This assumption is necessary because  $H_C$  data are not available for Ti-7.

It is noted that  $400 \mu\text{g/g}$ , the lower bound value observed for other titanium alloys (e.g., Ti-2 and Ti-12) by Shoesmith et al. (1997, pp. 7-11) was used as the critical hydrogen concentration for Ti-7 in REV 00 of this AMR. This value appears to be excessively conservative based on data reported by Ikeda and Quinn (1998a, p. 7).

#### 6.1.4 Hydrogen Absorption During Crevice Corrosion

Crevice corrosion, if it initiates, will propagate at a rate much higher than that of general corrosion. Crevice propagation, as mentioned in Section 6.1.1, can lead to failure by wall penetration as well as failure due to HIC because of hydrogen transported into the metal.

The most effective way to reduce hydrogen absorption is to choose a more crevice corrosion resistant alloy (Shoesmith et al. 1997, p. 15). Improvements in resistance to crevice corrosion have been attributed to alloying elements, which reinforce passivity. Susceptibility to crevice corrosion is eliminated through the alloying series Ti-2→Ti-12→Ti-16 (Shoesmith et al. 1997, p. 15). In accordance with CRWMS M&O (1999b, pp. 49, 51), the major additions are Mo (0.2–0.4%) and Ni (0.6–0.9%) for Ti-12 and Pd (0.04–0.08%) for Ti-16. Decreased crevice corrosion rates by adding alloying elements such as Mo and Ni to Ti-12 and Pd to Ti-16 are noted in Shoesmith et al. (1997, p.16), and discussed in recent reviews of Ti crevice corrosion behavior (Schutz 1988). The effect of deliberate alloying of Ti-12 with Ni and Mo, which segregate at grain boundaries and intermetallics, is to improve the susceptibility to crevice corrosion. Thus, while some crevice corrosion occurs in Ti-2, only minor crevice corrosion damage prior to repassivation occurs in Ti-12. The effect of adding Pd to ennoble titanium while avoiding segregation in Ti-16 further improves the susceptibility to crevice corrosion, and no crevice corrosion damage is observed in Ti-16. It can be seen from CRWMS M&O (1999b, pp. 45, 51) that the composition of Ti-7 is almost identical to that of Ti-16, but the Pd content is even higher in Ti-7 (0.12–0.25%) than in Ti-16 (0.04–0.08%). Therefore, Ti-7, like Ti-16, is not expected to suffer any crevice damage.

Crevice corrosion is one form of localized corrosion of a metal surface (ASM 1987, p. 4). The model developed by CRWMS M&O (2000a, Section 6.4.1) for the Ti-7 drip shield assumes that localized attack occurs only if the open circuit corrosion potential,  $E_{\text{corr}}$ , exceeds the threshold potential for breakdown of the passive film,  $E_{\text{critical}}$ . This is the universally accepted criterion for processes such as pitting. Experimental measurements reported by CRWMS M&O (2000a, Section 6.4.3) for  $E_{\text{corr}}$  and  $E_{\text{critical}}$  were obtained from various test environments expected in the repository. These test environments include simulated dilute water (SDW), simulated concentrated water (SCW), and simulated acidic concentrated water (SAW) at 30, 60, and 90°C, as well as simulated saturated water (SSW) at 100 and 120°C. SCW is about one thousand times more concentrated than J-13 well water and is slightly alkaline (pH~8). SAW is about one thousand times more concentrated than J-13 well water and is acidic (pH~2.7). J-13 well water (Harrar et al. 1990) is the groundwater from Yucca Mountain. The experimental measurements show that the threshold  $E_{\text{critical}}$  is consistently greater than  $E_{\text{corr}}$ . CRWMS M&O (2000a, Section 6.4.3) indicated that the difference,  $E_{\text{critical}} - E_{\text{corr}}$ , falls in the range from 995 mV to 1652 mV for the various test environments of SDW, SCW, SAW, and SSW at temperatures from 20–150°C.

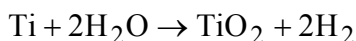
It is therefore concluded that hydrogen absorption during crevice corrosion or any other form of localized corrosion such as pitting may be ignored in the HIC model.



### 6.1.5 Hydrogen Absorption During General Passive Corrosion

According to Shoesmith et al. (1997, p. 15), there are two processes by which hydrogen could be produced, and possibly absorbed, under passive conditions: (1) direct absorption of hydrogen produced by water radiolysis and (2) absorption of atomic hydrogen produced by the corrosion process to produce oxide. The direct absorption of radiolytically produced hydrogen does not appear to be significant except at high dose rate ( $> 10^2$  Gy/h) and high temperature ( $> 150^\circ\text{C}$ ) (Shoesmith et al. 1997, p. 17). This condition is clearly unattainable under Yucca Mountain drip shield conditions and will not be considered, leaving the corrosion process as the only feasible source of hydrogen for absorption.

Under anoxic conditions, when passive corrosion should prevail, the corrosion potential for passive titanium must reside at a value at which water reduction can couple to titanium oxidation,



and, hence, must be at, or more negative than, the thermodynamic stability line for water. At such potentials, titanium hydrides are thermodynamically stable with respect to the metal. Consequently the passive film can be considered only as a transport barrier and not as an absolute barrier. The rate of hydrogen absorption at the corrosion potential will be controlled by the rate of the corrosion reaction, which dictates the rate of production of absorbable hydrogen. Since titanium oxide,  $\text{TiO}_2$ , is extremely stable and protective in the drip shield environment, the corrosion reaction will be effectively limited to an oxide film growth reaction.

While the rate of hydrogen production and, hence, absorption may be assumed directly proportional to the rate of film growth, the fraction of hydrogen absorption needs to be determined. Based on experimental measurements of Okada (1983), a value in the range of 0.005 to 0.015 may be adopted for  $f_h$ . These values represent the minimum and maximum values measured in the pH range 4 to 5 and can be considered conservative since they were measured on Ti-2 under constant applied current conditions with an applied current of  $0.5 \text{ mA/cm}^2$  at  $25^\circ\text{C}$  in sodium sulfate solutions at  $\text{pH} = 4$ . The electrode potential achieved during these experiments was  $-1.14 \text{ V}$  (vs. SCE), about 500 mV more negative than the threshold value of  $-0.6 \text{ V}$  (vs. SCE) for hydrogen absorption. Similar measurements on Pt and Ni-coated Ti-2 specimens gave a value of  $f_h$  only marginally higher under these conditions, a clear indication that the Pd-content of Ti-7 would not be expected to increase this value. The applied current density used was  $500 \mu\text{A/cm}^2$  compared to a value of  $1.45 \text{ nA/cm}^2$  calculated as the current that would flow at a general corrosion rate of 50 nm/year [the 70<sup>th</sup> percentile value of general corrosion rates measured for Ti-16 in the LTCTF at LLNL (CRWMS M&O 2000a, Section 6.5.4)].

The above mentioned values of  $f_h$  are appropriate for Ti-2 since the passive film is a good transport barrier to hydrogen absorption. Furthermore, the impermeability to hydrogen absorption will be improved by the period of dry thermal oxidation expected under repository conditions. The improved resistance to hydrogen absorption conferred by thermal oxidation has been documented by Mon (2002, Attachment III). For Ti-12, since Ni, in either  $\text{Ti}_2\text{Ni}$  intermetallics or in  $\beta$  phase, is present, a higher value would be more appropriate. For Ti-16 and

Ti-7 in which intermetallic formation is avoided, the values of 0.005 to 0.015 are most appropriate.

It may be pointed out that in the previous versions of this AMR (REV 00, ICN 01 and 02) a higher value of 0.1 was mentioned as the upper bound value of  $f_h$ . In this revision (REV 01), this value has been ruled out because of the following reasons:

1. It was adopted for calculations on Ti-12 (Shoesmith et al. 2000). However, Ti-12 is a  $\beta$ -alloy unlike Ti-16 and Ti-7, which are  $\alpha$ -alloys.
2. It was obtained from crevice corrosion studies on Ti-2. Since Ti-7 and Ti-16 are immune to crevice corrosion, the results of such studies conducted on Ti-2 are not applicable in the case of Ti-7 and Ti-16.

Based on a constant film growth rate and, hence, corrosion rate, Shoesmith et al. (1997, p. 22) indicated that the concentration of hydrogen in the metal,  $H_A$ , in  $\text{g/mm}^3$  can be calculated as a function of time of emplacement ( $t$  in years) from the expression:

$$H_A = 4(\rho_{\text{Ti}}/10^3)f_h R_{uc} t [M_{\text{Ti}}(d_o - R_{uc}t)]^{-1} \quad (\text{Eq. 1})$$

where

$H_A$  = hydrogen content ( $\text{g/mm}^3$ )

$\rho_{\text{Ti}}$  = density of Ti ( $\text{g/cm}^3$ ) = 4.5 (Weast 1978, p. B-177)

$f_h$  = fractional efficiency for absorption

$R_{uc}$  = rate of general passive corrosion (mm/year)

$t$  = time of emplacement in years

$M_{\text{Ti}}$  = atomic mass of Ti = 47.9 (Weast 1978, p. B-177)

$d_o$  = half of drip shield thickness

The fractional efficiency for absorption, based on previous discussion, is  $f_h = 0.015$  for Ti-7.

Considering a Ti-7 plate with  $1 \text{ mm}^2$  surface area, it is noted in Equation 1 that (1) the amount of hydrogen in grams produced by the general corrosion after  $t$  years of emplacement is  $4(\rho_{\text{Ti}}/10^3)R_{uc}t/M_{\text{Ti}}$  based on the reaction  $\text{Ti} + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 2\text{H}_2$ , (2) multiplication by the factor  $f_h$  converts the produced hydrogen into absorbed hydrogen, and (3) the remaining volume of Ti-7 alloy in  $\text{mm}^3$  is represented by  $(d_o - R_{uc}t)$ . The derivation of Equation 1 is based on a constant general corrosion rate. It was noted by CRWMS M&O (2000a, Sections 5.2, 6.3, and 6.5.2) that the assumption of constant corrosion rate is conservative, and less

conservative corrosion cases assume that the rate decays with time. It was also noted above that it is conservative to assume that all the hydrogen absorbed during general corrosion is retained within the remaining drip shield wall thickness as the general corrosion process proceeds. It is most likely that the majority of it will be removed by conversion to the more thermodynamically stable titanium oxide as corrosion progresses.

Using the relationship  $H (\mu\text{g of H/g of Ti}) = H (\text{g of H/mm}^3 \text{ of Ti})(1000)/(10^{-6}\rho_{\text{Ti}})$ , Equation 1 can be rewritten for  $H_A$  in  $\mu\text{g/g}$  as follows:

$$H_A = 4 \times 10^6 f_h R_{uc} t [M_{\text{Ti}} (d_o - R_{uc} t)]^{-1} \quad (\text{Eq. 2})$$

where

$H_A$  = hydrogen content ( $\mu\text{g/g}$ )

The rate of general passive corrosion,  $R_{uc}$ , can be calculated from the rate of oxide film thickness,  $R_{ox}$  by the following formula:

$$R_{uc} = R_{ox} (\rho_{ox} / M_{ox}) (\rho_{\text{Ti}} / M_{\text{Ti}})^{-1} \quad (\text{Eq. 3})$$

where

$\rho_{ox}$  = density of the oxide in  $\text{g/cm}^3$

$M_{ox}$  = molecular mass of the oxide

Since the value of  $(\rho_{ox} / M_{ox}) (\rho_{\text{Ti}} / M_{\text{Ti}})^{-1}$  is always greater than unity, it is conservative to assume that  $R_{uc} = R_{ox}$ .

The maximum general corrosion rate ( $R_{uc}$ ) reported in Section 4.1 has been used for the estimation of hydrogen concentration of the drip shield (see Section 6.2.3).

#### **6.1.6 Alternative Conceptual Model for Hydrogen-Induced Cracking Under General Passive Corrosion Conditions**

The present model, as described in Section 6.1.5, is based on the use of a general passive corrosion rate of titanium, which is constant over the lifetime of the drip shield. It is assumed that this process will be driven by the reaction of titanium with water to produce hydrogen and that a constant fraction of this hydrogen will be absorbed into the alloy and will eventually be precipitated as hydride (Assumptions 5.3 and 5.5).

Since measured corrosion rates (taken from LTCTF measurements at LLNL) are low, absorbed hydrogen will diffuse deeply into the alloy rather than accumulate at the corroding surface to be released as the corrosion front progresses into the metal. As a consequence, hydride formation

would occur uniformly throughout the wall thickness. Furthermore, it is assumed (Assumption 5.4) that, once absorbed, hydrogen would not be released, leading to a predicted long term acceleration in the rate of hydrogen accumulation as the volume of available metal is reduced by conversion to oxide. Since failure by HIC could occur once a critical hydrogen concentration ( $H_C$ ) is achieved, this acceleration leads to a very rapid achievement of this critical value and, hence, a very conservative prediction of failure times by HIC.

Key conservatisms adopted in this model are the following:

1. Corrosion of titanium will be driven by interaction with water to produce absorbable hydrogen (Assumption 5.3). Since conditions will be generally oxidizing, reaction will be predominantly with dissolved oxygen, a process that does not produce hydrogen.
2. Corrosion rates will be maintained constant over the lifetime of the drip shield (Assumption 5.4).
3. Hydrogen release by the conversion of the metal containing hydrogen to oxide as the corrosion progresses is negligible (Assumption 5.4).

An alternative, less conservative, and hence, more realistic conceptual model can be defined by relaxing conservatisms (2) and (3). The retention of the first conservatism is judicious, since titanium corrosion could be, at least partially, supported by water reduction in the concentrated saline environments possible as a consequence of evaporative concentration of seepage waters contacting the alloy surface. In these environments, the dissolved oxygen concentration would be low until temperatures cooled and salinity levels declined. This assumption is conservative since, with time, support of the general passive corrosion of titanium would be expected to shift from water reduction to oxygen reduction as the concentration of dissolved oxygen in the water increased with decreasing temperatures. As a consequence, the total amount of hydrogen produced, and hence the fraction absorbed, would decrease.

In this alternative model, the corrosion rate is given by the passive oxide film growth rate as before but is taken to decrease with time as the oxide thickens and becomes more impermeable to hydrogen. The rate of hydrogen absorption is directly proportional to the corrosion rate and the amount of hydrogen absorbed, calculated in the identical manner to that used in the performance assessment model. This means that this new model incorporates the same efficiency factor for hydrogen absorption. Consequently, the new model will predict a decrease in hydrogen absorption rate with a time-dependency equal to that for the decrease in corrosion rate.

As in the performance assessment (PA) model, the rate of diffusion of hydrogen in the titanium is taken to be rapid compared to the corrosion rate. Consequently, absorbed hydrogen will be dispersed throughout the full wall thickness; i.e., the concentration of hydrogen in the metal will be the same throughout. However, some hydrogen will be released as corrosion of the hydrogen-containing alloy continues. The rate of release will be proportional to the corrosion rate and to the concentration of hydrogen that exists in the metal at that time.

The criterion for failure remains the same as in the adopted model; i.e., failure could occur instantly once the amount of hydrogen in the material ( $H_A$ ) exceeds the critical value ( $H_C$ ). The value of  $H_C$  remains unchanged.

A schematic comparison of the original and the new conceptual models is given in Figures 2 and 3. The terms are defined as follows;

$R_{Corr}$ —corrosion rate of titanium

$R_{HA}$ —rate of hydrogen absorption into titanium

$f_h$ —fractional efficiency of hydrogen absorption

$R_{HR}$ —rate of absorbed hydrogen release due to continuing corrosion

$n_1$ —time exponent for the decrease in corrosion rate with time,  $t$

$k$ —oxide film growth constant

$J_H$ —flux of hydrogen in the metal at time  $t$ .

$(H_{Ti})_t$ —concentration of hydrogen in the metal at time  $t$ .

$H_C$ —critical hydrogen concentration in the metal for failure by HIC.

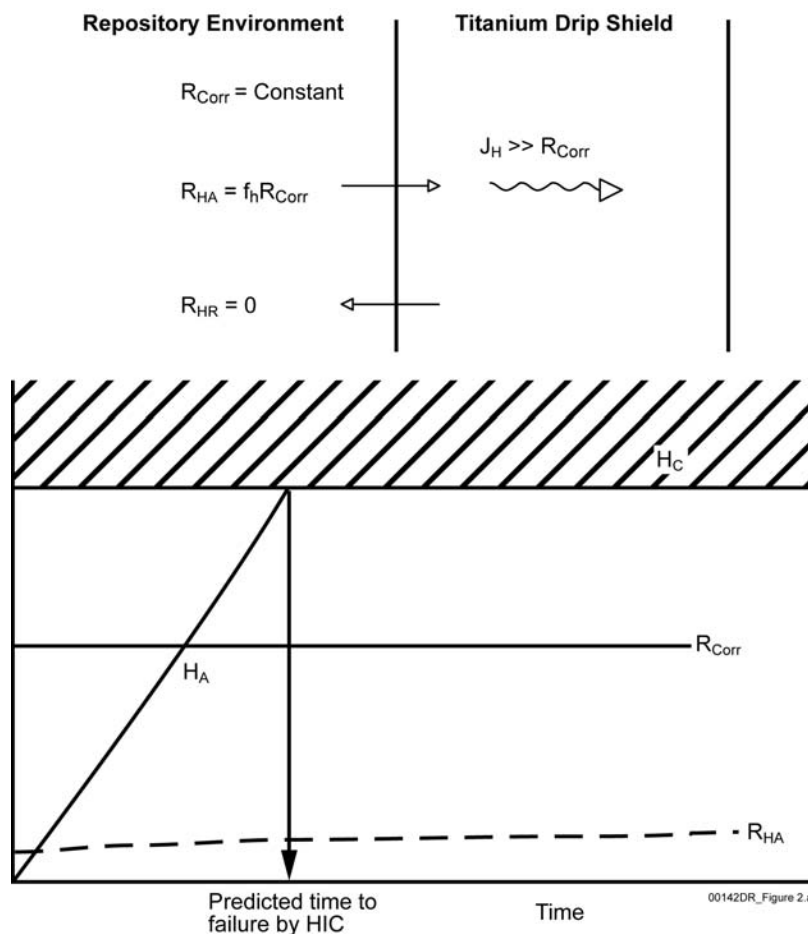


Figure 2. A Schematic Representation of the Current Performance Assessment Conceptual Model for Hydrogen Absorption During Passive General Corrosion of Titanium (refers to the mathematical model described in Section 6.1.5)

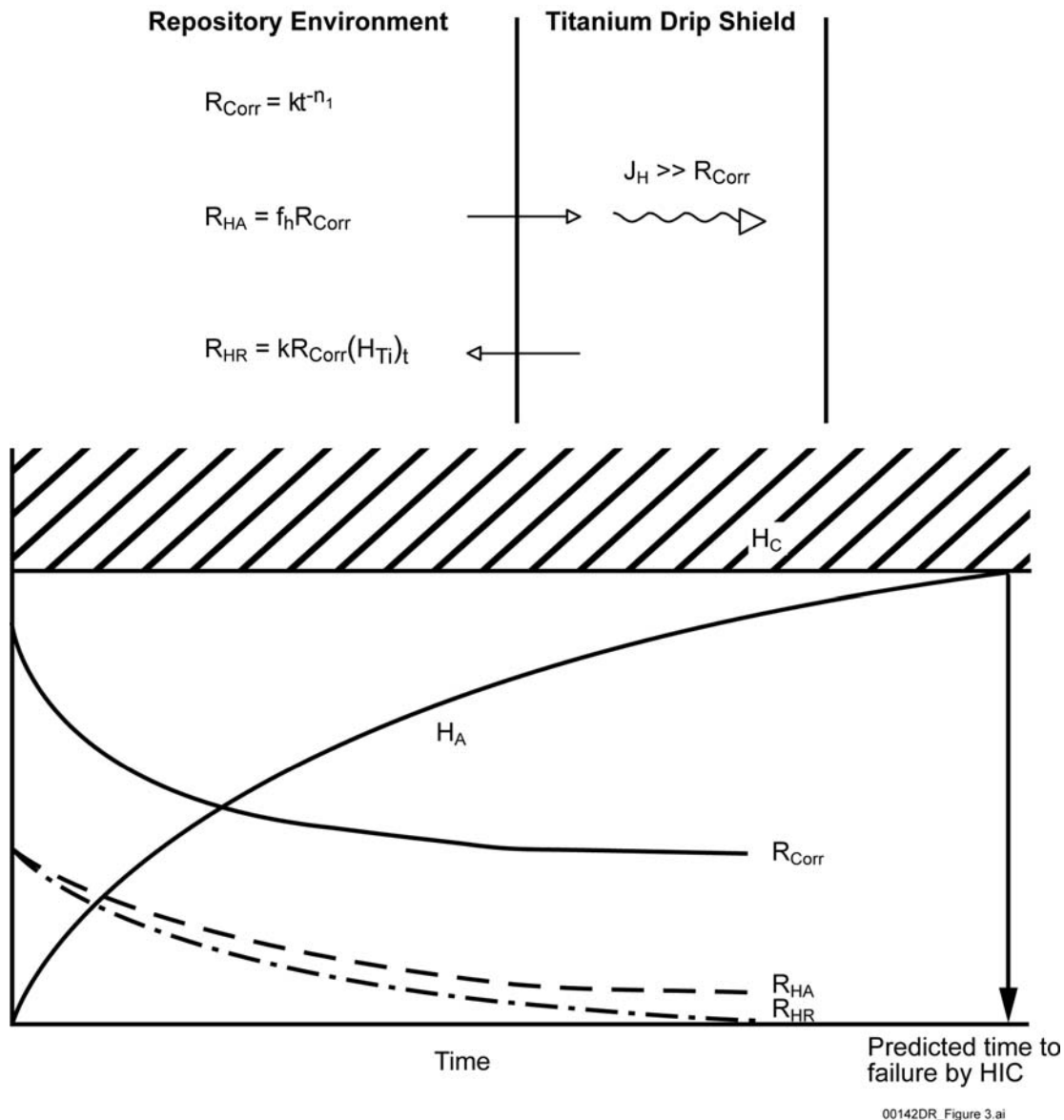


Figure 3. A Schematic Representation of the Alternate Performance Assessment Conceptual Model for Hydrogen Absorption During Passive General Corrosion of Titanium

The expected decrease in corrosion rate with time is the accepted mechanism for passive film growth in exposure environments in which the metal cation has a very low solubility as is the case for titanium in neutral to alkaline solutions (Baes and Mesmer 1986). Such a decrease in corrosion rate has been observed for Alloy 22 in tests conducted in the LTCTF at LLNL (CRWMS M&O 2000b, Section 6.9.1), and a similar behavior is anticipated for titanium.

Considerable electrochemical evidence exists to demonstrate that the rate of film growth decreases with time (Leitner et al. 1986; McAleer and Peter 1982; Nishimura and Kudo 1982; Beck 1982) according to the field-assisted ion-transport mechanism when subjected to a constant applied potential. While in these studies the potential driving oxide growth was applied electrochemically, a similar decrease in film growth rate with time would be expected to occur

due to the open-circuit polarization of titanium by a soluble redox reagent in an aqueous solution (e.g.,  $O_2$ ).

The universally-accepted structure for passive films, an inner protective barrier layer covered by an outer more porous, and hence less protective, hydrated layer, has been demonstrated for passive films on Ti (Pan et al. 1994), and a number of features of passive oxide film growth, besides an increase in thickness, have been shown to lead to a decrease in corrosion rate with time. Since defect transport, or ion transport via defects, is the primary mechanism for both film growth (Macdonald 1999) and film dissolution (Blackwood et al. 1988), a defect annealing process (Leitner et al. 1986) will lead to a decrease in corrosion rate. Such a decrease has been observed in neutral (pH ~5 to 6) hydrogen peroxide solutions (Fonseca and Barbosa 2001).

Studies in phosphate-buffered saline solutions (Pan et al. 1994) have shown that the incorporation of ionic species into the outer porous hydrated layer leads to a sealing, at least partially, of the porosity and an increase in film impedance, equivalent to a decrease in corrosion rate. Even under the aggressive conditions experienced in pulp and paper bleaching plants, the incorporation of  $Ca^{2+}$ ,  $Mg^{2+}$ , and particularly  $SiO_4^{2-}$ , into the oxide film have been shown to inhibit corrosion (Schutz and Xiao 1994; Whyllie et al. 1994). Based on these observations, it is reasonable to expect that the accumulation of silica on the surface will lead to a suppression of corrosion rate with time.

The use of a hydrogen absorption rate that is directly proportional to the corrosion rate, and, hence, can be determined by multiplying the corrosion rate by a time-independent absorption efficiency, is very conservative. When a coherent oxide is present on titanium, hydrogen absorption would not be expected until the passive film became a degenerate semiconductor, a condition requiring the application of a potential  $\leq -0.6V$  (vs SCE) (Shoesmith and Ikeda 1997). Conditions that would allow hydrogen absorption, therefore, require that one of the following conditions apply:

1. There is a source of polarization to a potential  $\leq -0.6V$
2. Destruction of the oxide occurs such that active conditions are achieved
3. The presence in the alloy of intermetallics can act as hydrogen absorption windows in the otherwise impermeable oxide (CRWMS M&O 2000c, Appendix A).

Since passive corrosion conditions prevail, condition (2) will not occur, and the cathodic polarization of titanium achieved by galvanic coupling to carbon steel sections within the repository drifts is modeled separately. Corrosion potential measurements on Ti-7 conducted in simulated Yucca Mountain groundwaters at General Electric Corporate Research and Development yielded a value of approximately -120 mV (vs. SCE) for immersion times greater than 2 days (BSC 2001, Section 3.3.3). Providing the potential remains within the band gap region of the  $TiO_2$  passive film ( $-0.6V$  to  $\sim 2.4V$  [vs. SCE]), then there is considerable published evidence to show that the oxide is an excellent barrier to hydrogen absorption (Been and Grauman 2000; Covington 1979; Shimogori et al. 1985). Clearly, a substantial period of dry

oxidation (under ventilated conditions) would be expected to improve the shield's resistance to hydrogen absorption.

This influence of the passive film in suppressing hydrogen absorption is also clearly demonstrated in the electrochemical measurements of Okada (1983) from whose data the value of the absorption efficiency used in the model was adopted. In this model, a value of 1.5% has been adopted for the efficiency. In reality, the actual value should be considerably less, since Okada's value was measured under cathodically polarized conditions, when the specimen potential would be very much lower than the threshold value of  $\sim -0.6$  V (vs. SCE), and hence, beyond the band gap region of the oxide.

Available evidence suggests that the presence of impurity Fe may increase the absorption of hydrogen by Ti-2 (Cotton 1970; Covington and Schutz 1981). Observed increases in hydrogen absorption by Ti-12 (Kim and Oriani 1987a) may also be attributed to the alloying additions, especially Ni and Mo. By contrast, no increase in hydrogen absorption was observed for Pd-containing alloys providing the pH was greater than  $\sim 4$  (Okada 1983). The key difference between these two categories is that the Ni in Ti-12 and the Fe (present as an impurity) in Ti-2 can form reactive (i.e., capable of sustaining both anodic and cathodic reactions) intermetallics ( $\text{Ti}_2\text{Ni}$ ,  $\text{Ti}_x\text{Fe}$ ) and/or  $\beta$ -phase, whereas intermetallic formation is rare in Ti-7, and  $\beta$ -phase formation does not occur.

The electrochemical results of Okada (1983) show that there was no difference in the hydrogen absorption efficiency for Ti-2 specimens and specimens coated with noble metal (Pt) providing  $\text{pH} \geq 4$  when a passive oxide will be present. This demonstrates that any tendency for the noble metal content of alloys Ti-7 and Ti-16 to catalyze hydrogen absorption (as observed under active, acidic conditions) (Fukuzuka et al. 1980) is masked when a passive oxide film is present.

Based on this discussion, the assumption that the efficiency for hydrogen absorption is constant and directly proportional to the corrosion rate is clearly conservative. The adoption of a value measured under polarization conditions equivalent to galvanic coupling makes the value for the efficiency conservative, since there is no reason to fear that the Pd content of Ti-7 will influence this value when the material is passive; i.e. in the neutral to alkaline pH range anticipated under Yucca Mountain conditions.

#### **6.1.7 Comparison Between the Current Performance Assessment Conceptual Model and the Alternative Conceptual Model for Hydrogen Absorption by Titanium During General Passive Corrosion**

A comparison of the current PA conceptual model as discussed in Section 6.1.5 with the ACM discussed in Section 6.1.6 identifies the following key differences and commonalities:

- In the PA model, the passive corrosion rate is assumed constant with time, whereas in the ACM it is allowed to decrease with exposure time.
- In the PA model, all the hydrogen absorbed is retained and not re-released as the corrosion front progresses into the alloy. By contrast, in the ACM some of the absorbed hydrogen is re-released as the corrosion front progresses into the alloy.



- In both models, the rate of hydrogen absorption is assumed directly proportional to the passive corrosion rate and the proportionality constant is a time-independent hydrogen absorption efficiency.
- In both models, the rate of transport of hydrogen in the alloy is assumed to be very fast compared to its rate of absorption. As a consequence, hydrogen in the alloy is uniformly distributed throughout the full wall thickness.

## 6.2 APPLICATION OF HIC MODEL TO DRIP SHIELD

### 6.2.1 Material

Titanium Grade 7 (Ti-7) (UNS R52400) is now being considered for construction of the drip shield for the waste package. As indicated in Section 1, this alloy consists of 0.3% Fe, 0.25% O, 0.12–0.25% Pd, 0.1% C, 0.03% N, 0.015% H, and 0.4% total residuals with the balance being Ti.

Both crevice corrosion and general passive corrosion will be accompanied by hydrogen production and, hence, possibly by the absorption of hydrogen into the metal. It has been concluded in Section 6.1.4 that hydrogen absorption during crevice corrosion will not be considered in the HIC model since crevice corrosion is essentially eliminated for Ti-7.

General corrosion rate for Ti-16 has been reported in Section 4.1. As may be noted in Table 1, the calculated maximum value for  $R_{uc}$  is  $2.82 \times 10^{-4}$  mm/year.

### 6.2.2 Determination of the Critical Hydrogen Concentration, $H_C$

As discussed in Section 6.1.3, Shoesmith et al. (1997, p. 11) concluded that a conservative value of  $H_C = 500$   $\mu\text{g/g}$  can be adopted as the critical hydrogen concentration in rolled plate material using Ti-2 and Ti-12 for predicting container lifetime. The lowest  $H_C$  value observed for Ti-2 and Ti-12 is  $\sim 400$   $\mu\text{g/g}$ . Ikeda and Quinn (1998a) indicated that  $H_C$  for Ti-16 is at least 1000  $\mu\text{g/g}$  and may be much greater.

The  $H_C$  value for Ti-7 is assumed to be at least 1000  $\mu\text{g/g}$ . This assumption is based on Assumption 5.1 and data reported by Ikeda and Quinn (1998a, p. 7), which, as indicated earlier, concluded that the  $H_C$  value for Ti-16 is between 1000 and 2000  $\mu\text{g/g}$ . This assumption is necessary because  $H_C$  data are not available for Ti-7.

It is noted that 400  $\mu\text{g/g}$ , the lower bound value observed for other titanium alloys (e.g., Ti-2 and Ti-12) by Shoesmith et al. (1997, pp. 7-11), was used as the critical hydrogen concentration for Ti-7 in REV 00 of this AMR. This value appears to be excessively conservative based on data reported by Ikeda and Quinn (1998a, p. 7).

### 6.2.3 Determination of Hydrogen Concentration

Based on Equation 2, the hydrogen concentration in the metal can be rewritten as follows:

$$H_A = 4 \times 10^6 f_h R_{uc} t [M_{Ti} (d_o - R_{uc} t)]^{-1}$$

where

$H_A$  = hydrogen content ( $\mu\text{g/g}$ )

$\rho_{Ti}$  = density of Ti in  $\text{g/cm}^3 = 4.5$  (Weast 1978, p. B-177)

$f_h$  = fractional efficiency for absorption

$R_{uc}$  = rate of general passive corrosion (mm/year)

$t$  = time of emplacement in years

$M_{Ti}$  = atomic mass of Ti = 47.9 (Weast 1978, p. B-177)

$d_o$  = half of drip shield thickness

More information about the model parameters are provided in Table 2.

Table 2. Model Inputs Used in Current Performance Assessment Model for Hydrogen Absorption During Passive General Corrosion of Titanium

Input Name	Input Description	Input Source (DTN if applicable)	Value or Distribution (Units)
$f_h$	Fractional efficiency for hydrogen absorption	Assumption 5.5	0.005 – 0.015
$\rho_{Ti}$	Density of Ti	Weast 1978, p. B-177	4.5 $\text{g/cm}^3$
$R_{uc}$	Rate of general passive corrosion (maximum)	DTNs: MO0003SPASUP02.003 LL990610605924.079	$3.88 \times 10^{-4}$ mm/year $1.76 \times 10^{-4}$ mm/year
$d_o$	Half of drip shield thickness	BSC 2003	7.5 mm
$t$	Time of emplacement	10 CFR 63.114(d)	10,000 years
$M_{Ti}$	Atomic mass of Ti	Weast 1978, p. B-177	47.9

As seen in Table 2, the fractional efficiency for hydrogen absorption is  $f_h = 0.015$  for Ti-7. The rate of general passive corrosion is  $R_{uc} = 2.82 \times 10^{-4}$  mm/year (maximum value) based on Sections 4.1 and 6.2.1. The time of emplacement is  $t = 10,000$  years. Half of the minimum wall thickness (15 mm) is used for  $d_o$ , i.e.,  $d_o = 7.5$  mm. Using half of the thickness of the drip shield

in calculations is equivalent to assuming that there is twice the surface area of Ti-7 available to absorb hydrogen because absorption can occur under as well as on top of the drip shield.

Conservative Estimate:

$$R_{uc} = 2.82 \times 10^{-4} \text{ mm/year}$$

$$f_h = 0.015$$

$$d_o = 7.5 \text{ mm}$$

$$t = 10,000 \text{ years}$$

From Equation 2,  $H_A = 755 \text{ } \mu\text{g/g} < H_C = 1000 \text{ } \mu\text{g/g}$ .

#### 6.2.4 Results

The analytical estimate presented in Section 6.2.3 based on Equation 2 indicated that there exists a big margin of safety for the drip shield against the effects of HIC. The hydrogen concentration in the drip shield at 10,000 years after emplacement is  $755 \text{ } \mu\text{g/g}$  resulting from a conservative estimate. The estimated hydrogen concentration is less than the critical hydrogen concentration of  $1000 \text{ } \mu\text{g/g}$  for Ti-7.

As discussed in Section 6.1.5, the current model is highly conservative in that it assumes all the hydrogen absorbed during general corrosion is retained within the remaining drip shield wall thickness as the general corrosion process proceeds. It is most likely that the majority of it will be removed by conversion to the more thermodynamically stable titanium oxide as corrosion progresses. With this conservative assumption, the hydrogen concentration in the drip shield increases continuously with time as the drip shield thickness (thus the volume of the remaining drip shield) is reduced by general corrosion. This hydrogen concentration increase from the thinning of the drip shield is in addition to the hydrogen pick-up from the general corrosion. With the current conservative model, the time for the hydrogen concentration in the drip shield to exceed the critical hydrogen concentration will always be before the time to failure of the drip shield by general corrosion.

As noted in Section 6.1.3, crack growth in the drip shield by HIC requires embrittlement of the drip shield (measured by the hydrogen concentration exceeding the critical hydrogen concentration) and applied stress. When the drip shield is subject to HIC, the failure will be by through-wall cracks, and the cracks are likely to be those generated by SCC. However, those cracks are self-limited and will be eventually plugged by corrosion products and scale deposits (CRWMS M&O 2000d, Section 6.5.5), especially calcite from available  $\text{CO}_2$  and silicates from ground waters (Section 6.3.2). Therefore, even when the drip shield is breached by through-wall cracks induced by HIC, the intended design function of the drip shield (i.e., preventing dripping water from directly contacting the underlying waste package) will not be compromised significantly from the HIC failure.

## 6.2.5 Parameter Uncertainties

**Uncertainties and Impacts on Model output**—Key input parameters in the model for hydrogen absorption during passive corrosion of titanium are  $R_{uc}$ ,  $f_h$  and  $H_C$ .

$R_{uc}$  was measured at the LTCTF of the LLNL using calibrated instruments and following quality assurance procedures. Therefore, the data used to determine  $R_{uc}$  is qualified “from origin”. The maximum value of  $R_{uc}$  (see Sections 4.1) was used for a conservative estimate of hydrogen concentration in the drip shield.

The constant value of  $f_h = 0.015$  adopted in the model was determined under extremely conservative conditions unachievable in the repository, and, therefore, constitutes a conservative upper limit for this parameter (Assumption 5.5). Consequently, the model predictions obtained using this value will also be conservative. Adoption of a value of  $f_h > 0.015$  (i.e., the value of 0.1 as discussed in Section 6.1.5) is not merited because it applies only to Ti-12, an alloy containing  $\beta$  phase. Since Ti-7 is an  $\alpha$ -alloy, which does not undergo crevice corrosion, the adoption of this higher value of 0.1 is not merited.

The value of 1000  $\mu\text{g/g}$  adopted for  $H_C$  is a conservative lower limit as discussed in Section 6.1.3. Measurements show the value could be as high as 2000  $\mu\text{g/g}$ . Adoption of a higher value, or a value distributed between 1000  $\mu\text{g/g}$  and 2000  $\mu\text{g/g}$ , would further decrease the probability of failure by HIC before 10,000 years.

The design parameters,  $d_0$  and  $t$ , are certain. Also,  $M_{Ti}$  and  $\rho_{Ti}$  are physical constants and therefore can be considered certain.

**Sources of Uncertainties**—A principal source of uncertainty is measurement error, particularly in the parameters  $R_{uc}$  and  $H_C$ . Another significant uncertainty is the lack of measurements on Ti-7, leading to the adoption of parameter values measured on the similar alloy Ti-16. The small database of measurements on the fracture toughness of Ti-7 (Ti-16) and the absence of information on the time-dependent decrease in the value of  $f_h$  have lead to the adoption of limiting conservative values for these parameters. This last uncertainty includes the uncertainty associated with variability in materials properties.

## 6.3 HYDROGEN INDUCED CRACKING OF TI-7 DUE TO GALVANIC COUPLING

### 6.3.1 Introduction

As indicated in Section 6.1.2, the three general conditions that must exist simultaneously for the hydrogen embrittlement of  $\alpha$  alloys are:

- A mechanism for generating hydrogen on a titanium surface
- A metal temperature above approximately 80°C (175°F)
- A solution pH less than 3 or greater than 12, or impressed potentials more negative than -0.7 V (SCE).

In accordance with Schutz and Thomas (1987, p. 673), one hydrogen-generation mechanism is the coupling of active metals such as zinc, magnesium, and aluminum to titanium leading to hydrogen uptake and eventual embrittlement of the titanium provided the other two conditions described above are met. A similar possible problem occurs when titanium is in galvanic contact with carbon steels. In a drip shield design without backfill, hydrogen generation may be caused by the galvanic couple between the titanium drip shield surface and ground supports (such as rock bolts, wire mesh, and steel liners used in the drift), which may fall onto the drip shield surface. Therefore, HIC or hydrogen embrittlement of the drip shield due to galvanic couple can not be ruled out since the conditions associated with metal temperature and water or moisture pH (or corrosion potential) as described above are certainly attainable under Yucca Mountain drip shield conditions.

### **6.3.2 Qualitative Assessment**

Given the expected evolution of ground waters potentially contacting the drip shield and the temperature regime within the repository (CRWMS M&O 2000a, Section 1.3), the required conditions for hydrogen absorption by the titanium drip shield are clearly present when galvanically coupled to sections of the steel components. If occurring while temperatures are high ( $\geq 80^{\circ}\text{C}$ ) and concentrated ground waters are present, then local hydrided “hot spots” are possible. These “hot spots” will only occur at those sites where both contact to carbon steel and the establishment of lasting (at least periodically) aqueous conditions are achieved. Their formation is likely to be promoted if the contact points coincide with abraded or scratched areas of the shield caused by the impact of collapsing sections of the ground support structure.

At higher temperature, hydrogen will be more rapidly absorbed and transported into the bulk structure to produce the hydride distribution required for extensive crack propagation. It is less likely that a hydride layer will be retained at the surface. As the temperature falls, the formation of surface hydrides becomes more likely as the rate of hydrogen transport into the bulk of the metal decreases. The formation of surface hydrides tends to reduce the efficiency of subsequent hydrogen absorption (Noel et al. 1996), and their presence has little effect on structural integrity.

The efficiency of Fe-Ti galvanic couples to cause hydrogen induced cracking of the titanium drip shield will be limited for a number of additional reasons:

1. The contact area is likely to be small and the anode to cathode area (area of steel and titanium, respectively) low. Since relatively low volumes of groundwater are likely to contact both metals simultaneously, anode to cathode areas close to one seem likely. If a couple with a small anode to cathode area ratio was established (i.e., a small piece of steel in contact with a large area of drip shield), then one would expect the couple to be more rapidly exhausted as the steel is consumed. Under these conditions, the amount of hydrogen absorbed would be limited. Future quantitative studies may be conducted to determine how much hydrogen would be liberated per unit mass of Fe, whether that much hydrogen could cause HIC in the adjacent Ti, and how fast hydrogen diffuses into the surrounding Ti to keep hydrogen low.

While temperatures are high ( $> 80^{\circ}\text{C}$ ), the intermittent nature of seepage dripping onto the drip shield should lead to only limited periods of the aqueous conditions required to sustain an active galvanic couple, thereby limiting hydrogen absorption while temperatures are high enough to drive hydrogen transport into the metal. For temperatures below  $80^{\circ}\text{C}$ , even galvanic polarization below the potential threshold of  $-0.6\text{ V}$  (vs. SCE) produces only innocuous surface hydride films (Schutz and Thomas 1987). Also, at these lower temperatures, the small amounts of dissolved  $\text{O}_2$  in the solutions forming the galvanic couples will make it very difficult to achieve polarization of the galvanic potential to less than  $-0.6\text{ V}$  (vs. SCE). Additionally, the intermittent wetting and drying cycles anticipated on the drip shield will lead to the ready formation of calcareous and mineral deposits, which are well known to dramatically suppress galvanic currents, thereby stifling hydrogen absorption (Lunde and Nyborg 1993).

2. Conditions in the repository will be oxidizing, making it less likely that the couple will sustain water reduction, and hence hydrogen absorption. However, at high temperatures in concentrated saline solutions, the amount of  $\text{O}_2$  dissolved in the solution forming the couple will probably be too low to displace water reduction as the primary cathodic reaction. However, the ferrous ion product of steel dissolution will be homogeneously oxidized to ferric species by dissolved  $\text{O}_2$ . If conditions remain neutral, this should lead to the formation of insoluble  $\text{Fe(III)}$  oxides/hydroxides, and little influence would be exerted on the galvanic couple. However, any tendency for acidification or the development of alkaline conditions will increase the ferric ion solubility. Under evaporative conditions, this could lead to quite high dissolved ferric ion concentrations and the establishment of a galvanic potential sufficiently positive to avoid hydrogen absorption into the titanium. It is well documented that only parts per million concentrations of multivalent transition metal cations such as  $\text{Fe(III)}$  are required to polarize titanium to passive conditions (Covington and Schutz 1981; Schutz and Thomas 1987) and ferric oxide deposits are passivating to Ti (Covington and Schutz 1981). Also, experimental evidence exists to show that galvanic currents (Hodgkiess et al. 1987) and the rate of hydrogen absorption (Lund and Nyborg 1993) will decrease with time as deposits (calcite from available  $\text{CO}_2$  and silicates from groundwaters) accumulate (Lund and Nyborg 1993; Hodgkiess et al. 1987).
3. In the proposed repository environment, both the Ti drip shield and steel component surfaces will experience a considerable period of dry high temperature ( $\geq 85^{\circ}\text{C}$  depending on whether the higher- or lower-temperature operating mode is adopted). This will leave both Ti and steel passivated (especially Ti) and avoid galvanic contact. While passivity on the steel may be subsequently disrupted, loss of passivity of the Ti drip shield will not be so readily achieved. Experimental evidence exists to show that air oxidation prevents hydrogen absorption by Ti even in aggressive (0.5% to 6% HCl) solutions at elevated temperatures ( $70^{\circ}\text{C}$  to  $250^{\circ}\text{C}$ ) (Mon 2002, Attachment III).
4. Titanium has a large tolerance for hydrogen (see Section 6.1.3 for critical hydrogen concentration), and substantial concentrations must be achieved before any degradation in fracture toughness is observed. This concentration level, as indicated in Section 6.1.3, has been measured to be in the range of 400 to 1000  $\mu\text{g.g}^{-1}$  for Ti-2 and Ti-12. Recent

measurements suggest that the tolerance for hydrogen of the Ti-16 (a titanium alloy very similar to Ti-7 in chemical composition) may be in the 1000 to 2000  $\mu\text{g.g}^{-1}$  range (Ikeda and Quinn 1998a, p. 7). According to Section 6.1.3, the critical hydrogen concentration for Ti-7 is 1000  $\mu\text{g.g}^{-1}$ .

Given the high critical hydrogen concentration, the large volume of available titanium in the drip shield into which absorbed hydrogen can diffuse, and other reasons stated above, hydrogen embrittlement of the Ti drip shield is highly unlikely.

### 6.3.3 Mathematical Model for Hydrogen Absorption and Diffusion in Drip Shield

As described in Section 6.3.2, hydrogen absorbed in the Ti-7 drip shield due to galvanic coupling with carbon steel may diffuse to the rest of the drip shield. A mathematical model is proposed in this section to predict the hydrogen concentration in the drip shield due to a galvanic couple between the drip shield and a carbon steel segment. The absorption and diffusion of hydrogen in the drip shield is a complex process. A mathematical model is possible only if a number of necessary assumptions are adopted. These assumptions (also mentioned in Section 5.7) are as follows:

- The drip shield is treated as an infinite plate. The thickness of the plate is denoted by  $H$ .
- The area of galvanically coupled wetted surface is considered circular in shape. While the actual geometry of the wetted area will undoubtedly have a more complex geometry, its representation by an equivalent circular area will not significantly alter the calculations described below. The radius of this circular wetted area is denoted by  $r_0$ .
- Hydrogen is absorbed into the drip shield through the contact plane and immediately reaches the other surface. The initial region of the drip shield with hydrogen absorption has the shape of a circular disk with a radius  $r_0$  and thickness  $H$ .
- As hydrogen starts to diffuse in the drip shield, the radius of the circular region will expand at a constant speed  $v$ . As a result, the radius  $r(t)$  of the circular disk at a time  $t$  is expressed by the following equation:

$$r(t) = r_0 + v t \quad (\text{Eq. 4})$$

The amount of hydrogen (in g or mg, for example),  $Q(t)$ , absorbed in the drip shield at a time  $t$ , therefore, is:

$$Q(t) = \lambda \left( \rho_{\text{Ti}} \pi r_0^2 \right) H t + \int_{\tau=0}^{\tau=t} \lambda \rho_{\text{Ti}} [2\pi r(\tau)] H (t - \tau) d\tau \quad (\text{Eq. 5})$$

where  $\lambda$  is the hydrogen absorption rate, in ppm (or  $\mu\text{g/g}$ ) /day, for example, and  $\rho_{\text{Ti}}$  is the mass density of the Ti-7 drip shield (see Section 6.1.5).

Based on the reaction:  $2\text{Fe} + 3\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 3\text{H}_2$ , the maximum amount of hydrogen, formed by corrosion of the carbon steel, that can be absorbed by titanium is:

$$Q_{\max} = f_{\text{Fe}} 3W / M_{\text{Fe}} \quad (\text{Eq. 6})$$

where  $W$  is the mass of the carbon steel segment,  $f_{\text{Fe}}$  is the fraction of hydrogen produced by oxidation of the total mass of carbon steel, and  $M_{\text{Fe}}$  is the atomic mass of Fe.

If  $t_{\max}$  is the time when  $Q(t)$  reaches  $Q_{\max}$ ,  $t_{\max}$  can be obtained by solving for the following equation:

$$Q_{\max} = \lambda \left( \rho_{\text{Ti}} \pi r_o^2 \right) H t_{\max} + \int_{\tau=0}^{\tau=t_{\max}} \lambda \rho_{\text{Ti}} [2\pi r(\tau)] H (t_{\max} - \tau) d\tau \quad (\text{Eq. 7})$$

Using Eq. 4, Eq. 7 can be written as:

$$Q_{\max} = \lambda \rho_{\text{Ti}} \pi H \left( r_o^2 t_{\max} + r_o v t_{\max}^2 + \frac{v^2 t_{\max}^3}{3} \right) \quad (\text{Eq. 8})$$

The maximum hydrogen concentration  $H_A(r_o)$  in ppm (or  $\mu\text{g/g}$ ), for example, will be in the region of the drip shield beneath the initial contact area and at the time  $t_{\max}$ , i.e.,

$$H_A(r_o) = \lambda t_{\max} \quad (\text{Eq. 9})$$

The hydrogen concentration  $H_A(r)$  tends to be reduced at locations with a radius  $r$  from the center of the initial contact area, i.e.,

$$H_A(r) = \lambda \left( t_{\max} - \frac{r - r_o}{v} \right) \quad \text{for} \quad r_o \leq r \leq r(t_{\max}) \quad (\text{Eq. 10})$$

At  $t > t_{\max}$ ,  $H_A(r)$  will start to decline as the hydrogen diffusion continues and the source of hydrogen exhausts.

As a numerical example, the following input data are considered:

$H$  = Ti-7 plate thickness = 15 mm

$r_o$  = radius of the initial contact area = 50.8 mm (2 in.)

$\rho_{\text{Ti}}$  = density of Ti-7 =  $4.5 \times 10^6 \mu\text{g/cm}^3$

$f_{\text{Fe}}$  = fraction of hydrogen available for absorption by Ti-7 drip shield = 0.015 (refers to Assumption 5.5)



$W = \text{mass of carbon steel} = 22.727 \times 10^3 \text{ g (50 lb.)}$

$M_{\text{Fe}} = \text{atomic mass of Fe} = 55.847 \text{ (Weast 1978, p. B-177)}$

The corrosion potential of carbon steel is estimated to be about -0.6 V (SCE), and a galvanic couple would polarize Ti down to that level. Based on Shoesmith et al. (1995, Figure 19) and Murai et al. (1977, Figure 5), the hydrogen absorption rate,  $\lambda$ , for Ti-7 would be about 0.5  $\mu\text{g/g/day}$ . Inspection of Figure 5 in Murai et al. (1977) shows that the maximum value of  $\lambda$  measured in the potential range -0.6 V to -1.0 V (SCE) is  $\sim 0.7 \mu\text{g/g/day}$ . Therefore, this value is adopted as the maximum  $\lambda$  value in this sensitivity study. No data are available for the hydrogen diffusion rate,  $v$ , of Ti-7. For the base case of the numerical example, the values used for  $\lambda$  and  $v$  are, respectively, 0.5  $\mu\text{g/g/day}$  and 1mm/day. For the parametric study,  $\lambda = 0.5, 0.7 \mu\text{g/g/day}$ , and  $v = 1, 2, 3 \text{ mm/day}$  are considered, and plots of hydrogen concentration versus distance from the original contact area are shown in Figure 4. It can be seen that, in all cases of the parametric study, the hydrogen concentration does not exceed the critical hydrogen concentration of 1000  $\mu\text{g/g}$  for Ti-7 by a rather comfortable margin. The results of the parametric study appear to be consistent with the qualitative assessment presented in Section 6.3.2. The choice of the mathematical model and the value of  $\lambda$  appear to be reasonable and conservative. The value of  $v$  is high but would also appear to be reasonable, since it ignores the probability that the hydrogen will be retained at the Ti surface and the efficiency of absorption would then decrease. The calculation can be considered bounding since all the features likely to suppress hydrogen absorption are ignored in the calculation. These features are summarized above in section 6.3.2.

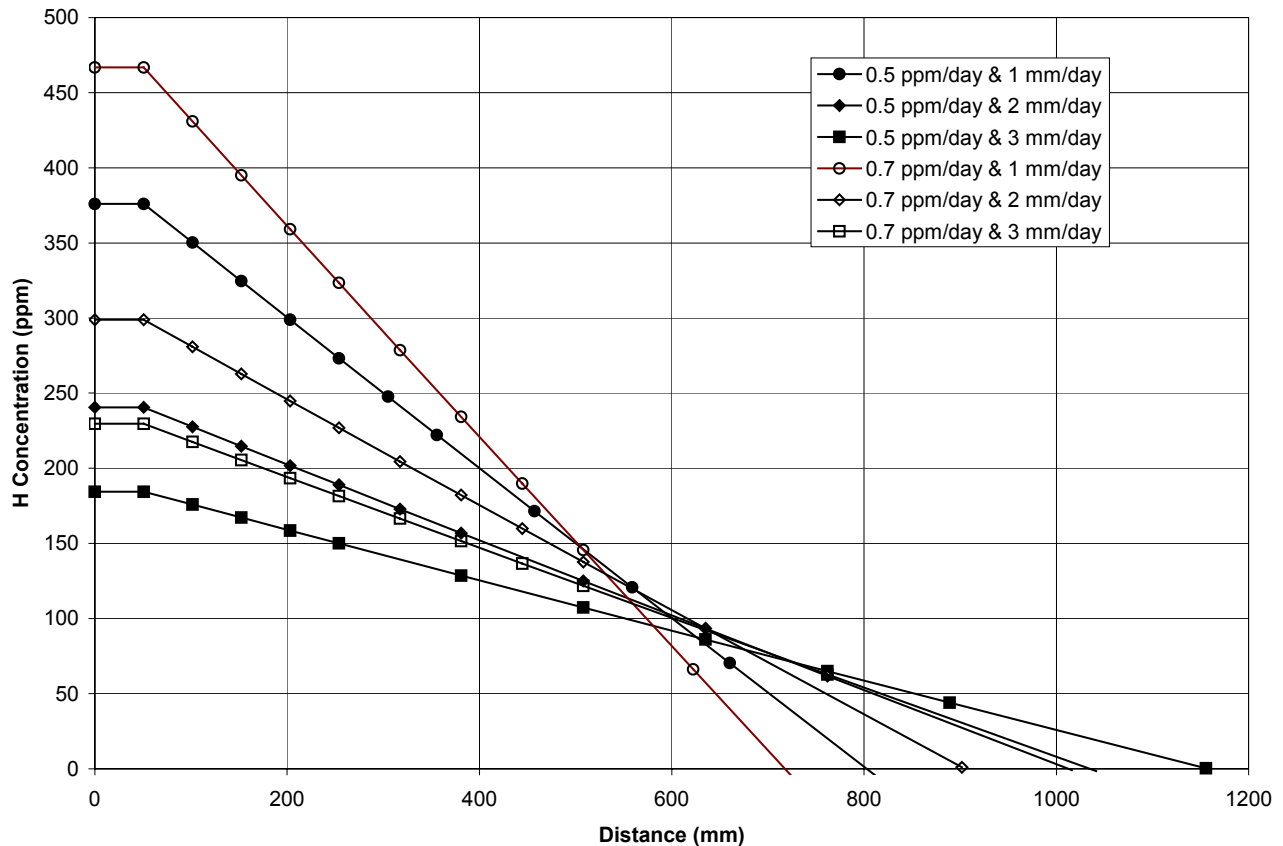


Figure 4. Hydrogen Concentration in Drip Shield Versus Distance from Contact Area

### 6.3.4 Parameter Uncertainties and Sensitivity Analyses

**Uncertainties and Impacts of Uncertainties on Model Outputs**—The key parameters in this model are the mass of steel ( $W$ ), the radius of the initial contact area ( $r_0$ ), the fraction of hydrogen absorbed ( $f_{Fe}$ ), the critical hydrogen concentration,  $H_C$ , the hydrogen absorption rate ( $\lambda$ ) and the hydrogen diffusion rate ( $v$ ).

The values of  $W$  and  $r_0$  adopted will both influence the analysis but include uncertainties that cannot be quantified. The value of  $W = 22.727$  kg (50 lbs) for the mass of steel available for consumption in a single galvanic couple is a conservative limit, since it ignores the stifling of coupled conditions by the evolving local environment at the coupled site, as discussed in Section 6.3.2.

The choice of a value of  $r_0 \sim 50.8$  mm (2 in.) is a realistic but uncertain value. The size of the contact area will be decided by the amount and distribution of aqueous solution trapped at the carbon steel/Ti-7 contact site, not the actual metal to metal contact area. The loss of wet contact by evaporation, gravitational flow and capillary absorption into accumulating corrosion products

will be the primary influence limiting  $r_0$ . Although it is difficult to quantify it is unlikely that a large uncertainty is associated with the chosen value.

The value of  $\lambda$ , the hydrogen absorption rate, is a very conservative upper limit since it ignores the observed decrease in absorption rate with time as discussed in Section 6.3.5. As a consequence, the model will predict a conservative rapid accumulation of hydrogen. To be consistent with this constant high rate of hydrogen absorption it was necessary to also assume a fast rate of hydrogen transport ( $v$ ) within the Ti-7 (Assumption 5.7). The values of  $v$  chosen were arbitrary but much higher than the transport rates that would be calculated from measured diffusion coefficients of hydrogen in Ti. This conservatism is partially offset by allowing lateral hydrogen transport away from the contact area.

The conservative natures of the parameters  $H_C$  and  $f_{Fe}$  (equivalent to  $f_h$ ) have been discussed in Section 6.2.5.

**Sources of Uncertainties**—Any event sequence(s) causing variations in the mass of the steel anode, and the anode and cathode areas will alter the model output and serve as sources of uncertainty.

### 6.3.5 Alternative Conceptual Model For HIC Under Galvanically-Coupled Conditions

An additional source of hydrogen that could lead to its absorption by the drip shield and, hence, possibly to shield failure by HIC, is wet contact between the drip shield and carbon steel ground supports components (e.g., rock bolts, wire mesh and steel drift liners) within the repository drifts.

In the PA model, as noted in Section 6.3.3, the galvanic coupling supports corrosion of the carbon steel according to the reaction



and a certain fraction of the hydrogen, produced on the drip shield surface, is then absorbed into the titanium. This fraction, expressed as an absorption efficiency, is the same as that absorbed under non-galvanically-coupled conditions and used in the model for hydrogen absorption during general passive corrosion. This is appropriate since the absorption efficiency was measured under cathodically polarized conditions akin to those which will prevail when the titanium is galvanically coupled. While this makes the use of this efficiency very conservative for general passive corrosion, it is more realistic for galvanically-coupled conditions.

Once absorbed, the hydrogen rapidly diffuses through the full wall thickness of the shield and, with time, diffuses laterally within the drip shield wall to adjacent locations not in direct galvanic contact with the steel. Corrosion of the carbon steel, and hence hydrogen absorption by titanium, stop once all the available contacting steel has been consumed. The criterion for failure is the same as that used in the general passive corrosion model, i.e., failure by HIC is instantaneous once the concentration of hydrogen in the titanium exceeds the critical value,  $H_C$ .

This model contains a number of key conservatisms mentioned below:

1. The possible extent of galvanic corrosion will be limited by the small area of contact between the two metals, the low cathode-to-anode ratio (Ti/Fe) which is likely to approach one, the low probability that the point of galvanic contact will simultaneously experience seepage drips, the inability of the site to remain wet due to run-off, and the stifling of steel corrosion by the accumulation of iron oxide corrosion products. In view of these limitations, the assumption that a considerable mass of steel (up to 50 lbs) could be consumed by galvanic corrosion is very conservative (Assumption 5.6).
2. Once absorbed, hydrogen will diffuse rapidly within the metal (Assumption 5.7, third bullet). However, practically measured diffusion coefficients for hydrogen in  $\alpha$ -titanium are low and thermally-activated in the normal Arrhenius manner (Phillips et al. 1974).
3. The absorption efficiency for hydrogen remains constant throughout the duration of the galvanic corrosion process (Assumption 5.5). Considerable evidence exists to show that, under galvanically coupled conditions, a surface hydride layer is formed (Noel et al. 1996; Mon 2002, Attachment II; Tomari et al. 1999) and, as a consequence, the efficiency for hydrogen absorption decreases substantially with time.

An alternative, less conservative, and hence, more realistic model can be defined by incorporating a flux term for hydrogen absorption in the alloy and using a time-dependent absorption efficiency. This is equivalent to relaxing the conservatisms in (2) and (3) above.

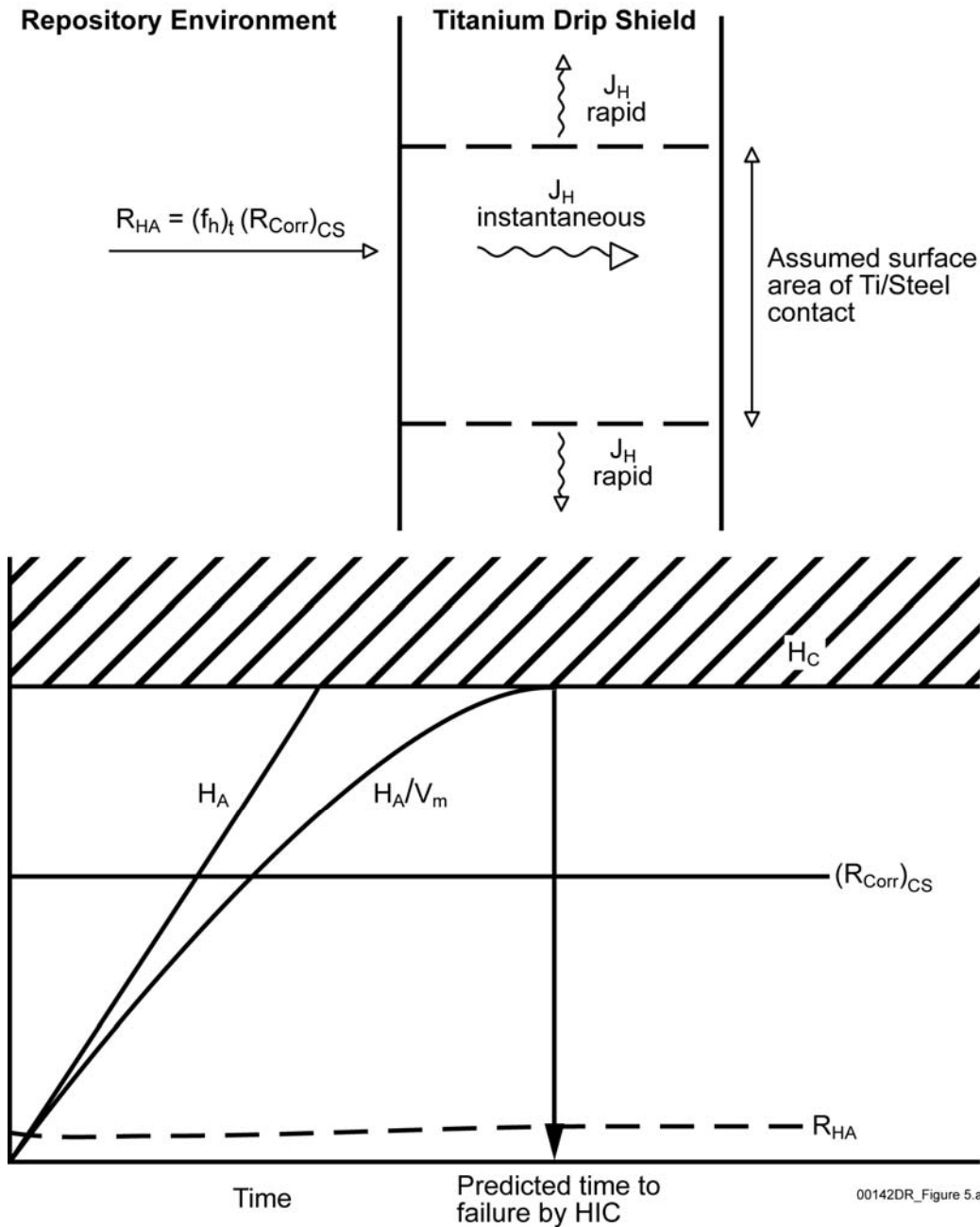
The rate of hydrogen production is taken as constant and equal to the rate of carbon steel corrosion until the amount of available steel is consumed, after which no further hydrogen absorption due to galvanic coupling occurs. However, since a considerable literature exists to show that the rate of hydrogen absorption follows a parabolic relationship (e.g., Tomari et al. 1999), the absorption efficiency is taken to decrease with time. This acknowledges that the amount of hydrogen that can absorb is limited to the amount required to form a surface hydride layer.

The flux of hydrogen within the material is calculated using Fick's laws with a diffusion coefficient, which is dependent on temperature according to Arrhenius' Law as shown in Figure 6 as  $J_H$ . As a consequence, a steady-state is eventually established in which the rate of hydrogen absorption into the surface of the titanium is controlled by the temperature-dependent flux of hydrogen from the surface into the bulk of the material. Lateral diffusion of hydrogen to sites not in direct galvanic contact with the titanium is ignored.

A schematic comparison of these two models is given in Figures 5 and 6. This comparison emphasizes the conservatisms in the adopted PA model compared to the alternative conceptual model. The additional terms are defined as follows:

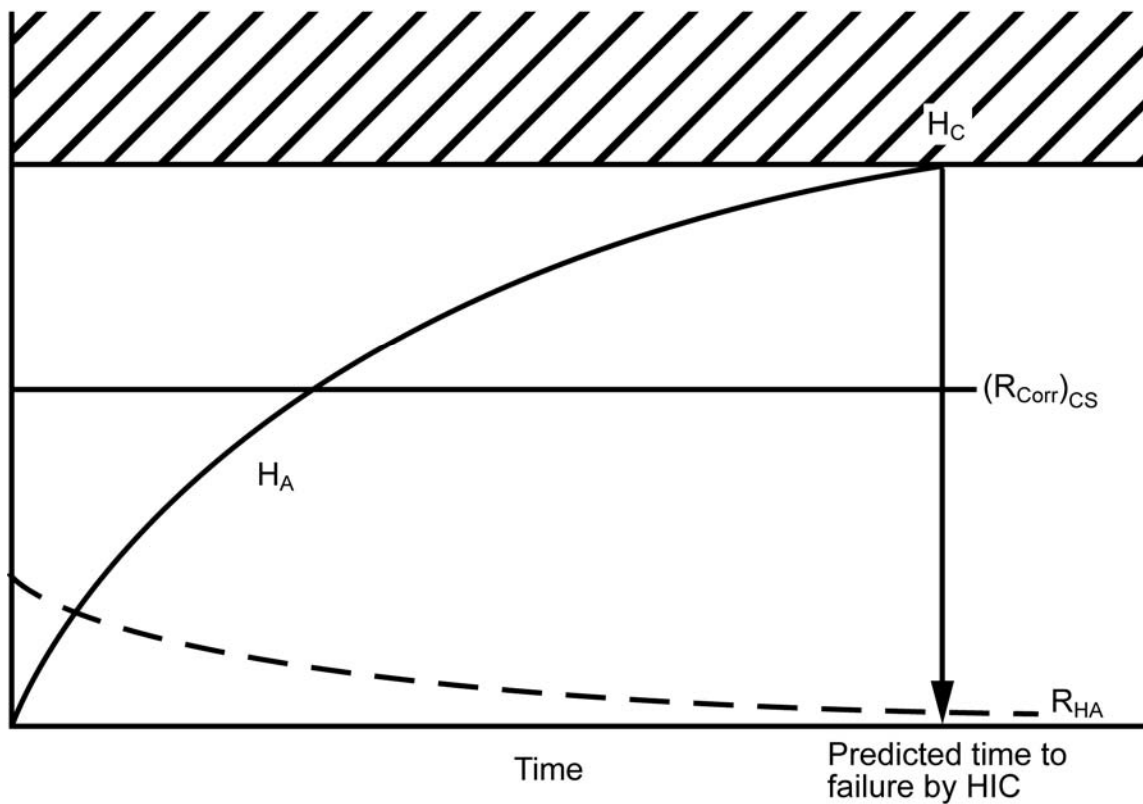
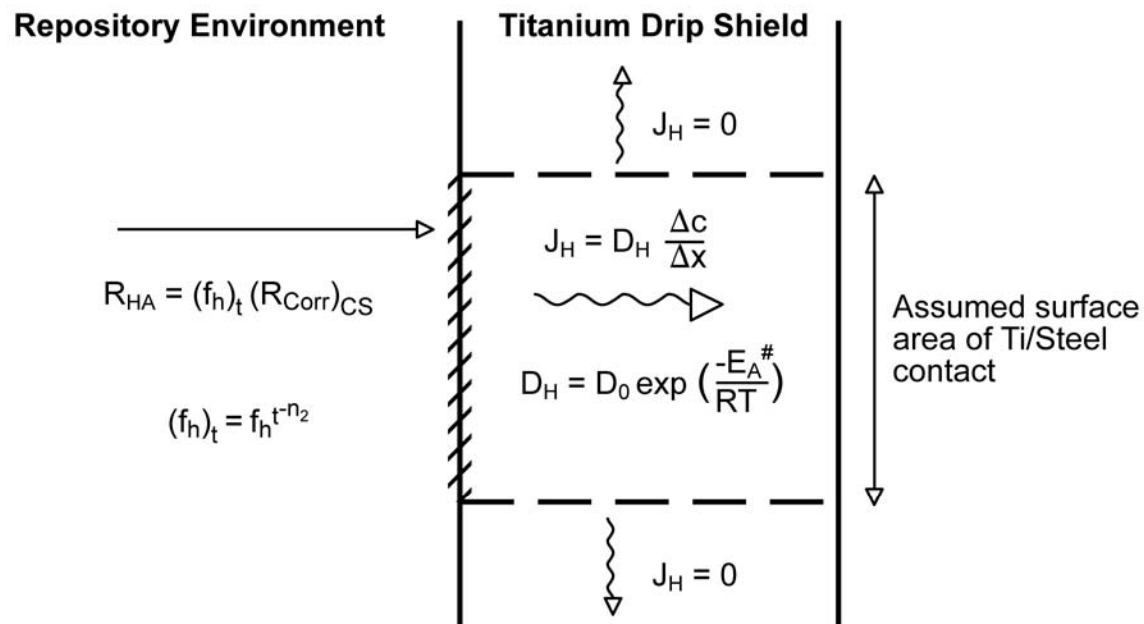
- $(R_{\text{Corr}})_{\text{CS}}$ —corrosion rate of carbon steel galvanically-coupled to titanium
- $(f_h)_t$ —the time-dependent fractional absorption efficiency for hydrogen in to titanium
- $n_2$ —time exponent for the decrease in  $(f_h)_t$  as a function of time
- $D_H$ —temperature-dependent diffusion coefficient of hydrogen in  $\alpha$ -titanium

$D_0$ —diffusion coefficient of hydrogen in  $\alpha$ -titanium at 25°C  
 $\Delta c/\Delta x$ —concentration gradient of hydrogen in the titanium defined by Fick's laws  
 $E_A^\#$ —activation energy for hydrogen diffusion in  $\alpha$ -titanium  
 $V_m$ —volume of titanium containing hydrogen  
 $R$ —gas constant  
 $T$ —temperature.



NOTE: CS = carbon steel.

Figure 5. A Schematic Representation of the Current Performance Assessment Conceptual Model for Hydrogen Absorption (HA) During Galvanic Coupling of Titanium (refers to the mathematical model described in Section 6.3.3)



00142DR\_Figure 6a.ai

NOTE: CS = carbon steel.

Figure 6. A Schematic Representation of the Alternate Performance Assessment Conceptual Model for Hydrogen Absorption During Galvanic Coupling of Titanium

A number of studies have been published which clearly show the rate of hydrogen absorption decreases parabolically with time (Kim and Oriani 1987a; Noel et al. 1996; Phillips et al. 1974; Tomari et al. 1999; Foroulis 1980). Since all of these studies were conducted under cathodically polarized conditions akin to, or much more polarized than, those anticipated as a consequence of galvanic coupling to carbon steel, the use of a decreasing absorption efficiency in our model is appropriate. In all cases the storage of hydrogen in the surface of the titanium was clearly demonstrated by the identification of a surface hydride layer. Since the majority of these studies were performed in acidic solutions with large applied current densities, the hydride layers were much thicker (many microns) than would be anticipated for galvanic coupling conditions under Yucca Mountain conditions.

Tomari et al. (1999) and Phillips et al. (1974) showed that the parabolic relationship for hydrogen absorption possessed a  $t^{1/2}$  time-dependence consistent with the form adopted in the model; i.e., the hydrogen absorption process is controlled by the transport of hydrogen from the surface layer into the bulk of the alloy. The presence of the surface hydride, or the storage of hydrogen in a concentrated surface layer, was confirmed optically (Noel et al. 1996; Phillips et al. 1974), by glow discharge spectroscopy (Mon 2002, Attachment II) and by SIMS depth profiling (Tomari et al. 1999). Glow discharge spectroscopy was also used to show the change in distribution of hydrogen in the alloy as a consequence of transport over time.

Tomari et al (1999) showed that Ti-2 and Ti-17 (Ti-16 with a slightly higher oxygen concentration) exhibited effectively identical parabolic relationships for hydrogen absorption, indicating that the Pd alloy content had no measurable influence on either hydrogen absorption or its subsequent transport within the alloy. This is consistent with the conclusion (above) that any possible influence of the Pd content of the titanium is masked under passive conditions.

Based on similar studies performed as a function of temperature by Phillips et al. (1974) and Mon 2002, Attachment II), a diffusion coefficient for hydrogen transport in titanium ( $2-4 \times 10^{-12}$  cm<sup>2</sup>/s) and an activation energy of  $60 \pm 3.4$  kJ/mol were determined.

Based on this discussion, the use of a time-dependent hydrogen absorption efficiency, which decreases with time, is appropriate. The use of a constant absorption efficiency in the PA model makes that model conservative by comparison to this alternative model. The adoption of a  $t^{1/2}$  time dependency for this efficiency is also justified. Since well-documented values exist for the diffusion coefficient of hydrogen in titanium and the activation energy for this diffusion process, the form of the model is appropriate.

### **6.3.6 Comparison between the Current Performance Assessment Conceptual Model and the Alternative Conceptual Model for Hydrogen Absorption During Galvanic Coupling**

A comparison of the current PA conceptual model for hydrogen absorption as discussed in Section 6.3.3 with the ACM discussed in Section 6.3.5 reveals the following commonalities and differences:

- In both models, the rate of hydrogen absorption is directly proportional to the rate of carbon steel corrosion.

- In both models, the extent of carbon steel corrosion is limited by assuming a limited mass of steel is available by galvanic coupling.
- In both models, an arbitrary, but reasonable, area of wetted contact between the steel and the Ti-7 is assumed.
- In the PA model, the efficiency for hydrogen absorption is assumed to be constant with time, whereas, in the ACM model it is allowed to decrease with time as hydrogen accumulates in the surface of the Ti.
- In the PA model, the absorbed hydrogen is rapidly transported through the full wall thickness. In the ACM model, hydrogen diffuses through the Ti-7 at a rate controlled by the measured temperature dependent diffusion coefficient.
- In the PA model, hydrogen is allowed to diffuse laterally along the wall of the drip shield. In the ACM model lateral diffusion is not allowed.

### 6.3.7 Worst Case Considerations

As a worst case scenario, it is considered that the majority portion of the hydrogen generated by the section of carbon steel will be absorbed by the drip shield and that the absorbed hydrogen will be retained in the vicinity of the contact area and not be diffused to the rest of the drip shield. In this case, there may be a local embrittlement of the drip shield in the contact area. It is further considered that the contact area is impacted by a rock fall, and residual stress and a crack are initiated. As a result, a fast brittle fracture is possible if the stress intensity factor calculated from the residual stress and the crack size exceeds the fast fracture stress intensity factor  $K_H$ , which tends to have a lower value than the critical slow crack growth stress intensity factor  $K_S$  (also called fracture toughness) as indicated in Figure 1.

Calculated stress intensity factors due to rock fall in the drip shield are listed in CRWMS M&O (2000d, Attachment II) for various crack sizes (depths). Based on CRWMS M&O (2000d), an initial crack depth of 50  $\mu\text{m}$  (i.e., the maximum incipient crack size, based on CRWMS M&O 2000d, Section 6.5.2) can be considered. The equivalent stress intensity factor, on the basis of CRWMS M&O (2000d, Attachment II), is  $< 5 \text{ MPa}\cdot\text{m}^{1/2}$ . From CRWMS M&O (2000d, Figure 27), it can be seen that the fracture toughness  $K_S$  for Ti-7 should be at least  $30 \text{ MPa}\cdot\text{m}^{1/2}$ . Noting  $K_H \sim 1/3 K_S$  from Figure 8 of Clarke et al. (1994), brittle fracture of the drip shield would require a value of  $K_H = 10 \text{ MPa}\cdot\text{m}^{1/2}$ . Since this value of  $K_H$  is greater than  $5 \text{ MPa}\cdot\text{m}^{1/2}$ , brittle fracture due to hydrogen embrittlement would not be a problem for the drip shield subjected to galvanic coupling with a section of the carbon steel ground support.

Even though fast brittle fracture does occur and the surface crack turns into a through-wall crack, the length of the crack will still be limited because the surrounding area of the drip shield is not embrittled by hydrogen. The crack opening will eventually be plugged by corrosion product (CRWMS M&O 2000d, Section 6.5.5).



## 7. MODEL VALIDATION

Models described in this AMR are expected to predict accurately and precisely the hydrogen concentration in the Ti-7 drip shield for a period of at least 10,000 years. This extraordinarily long time factor makes it extremely difficult to validate these models in the usual way, i.e., by comparison of model predicted values with those observed experimentally for the whole range of time (ASTM C 1174, Sections 19.3 and 20.4). Consequently, a different approach was adopted in the TWP (BSC 2002) for the validation of these models. According to this new approach, these models were validated by validating the input parameter values used and comparing these parameters and model predictions to available peer reviewed and qualified project data. The medium level of confidence in the titanium HIC models, as mentioned in the TWP, was obtained by validating three key model parameters, e.g., the passive corrosion rate, the critical hydrogen concentration, and the hydrogen absorption efficiency. In order to build further confidence in these models, the model output values were corroborated with those available in the peer reviewed scientific literature. In addition, four criteria were developed and documented in the TWP (BSC 2002) to ensure that the required level of confidence in these models for the models' stated purposes has been achieved. They are: (1) the critical hydrogen concentration of the grade-7 titanium alloy is consistent with the literature; (2) the general corrosion rates used in the model are consistent with the literature; (3) a comparison of the rates of hydrogen absorption calculated by the model to the calculated fluxes of absorbed hydrogen within the alloy demonstrates that the assumption that all hydrogen absorbed remains in the alloy is conservative; and (4) the hydrogen contents for grade-7 titanium and similar alloys predicted by the model are consistent with the literature. A detailed description of the validation of HIC models in light of these criteria is given below.

### 7.1 VALIDATION OF MODEL FOR HYDROGEN ABSORPTION DURING GENERAL PASSIVE CORROSION OF TITANIUM

According to TWP (BSC 2002), model validation will involve meeting the selected criteria as discussed below:

#### Criterion 1

*Is the critical hydrogen content ( $H_C$ ) of the Grade-7 titanium alloy (Ti-7) used by the model consistent with the results of mechanical tests published in the peer-reviewed literature?*

Using the slow strain rate technique on precracked compact tension specimens precharged with known amounts of hydrogen, it has been shown that the fracture toughness of Grades -2, -12, and -16 (Ti-2, Ti-12, Ti-16) are not significantly altered until their hydrogen levels exceed critical values 400  $\mu\text{g/g}$ , 400  $\mu\text{g/g}$ , and >1000  $\mu\text{g/g}$ , respectively. It should be noted that these values are lower limiting values, not mean values and, hence, are conservative. These values, and the details of their measurement, are published in the peer-reviewed literature (Clarke et al. 1994, 1997; Shoesmith et al. 2000; Ikeda et al. 2000). The model assumes that, for Ti-7, the minimum  $H_C$  value of 1000  $\mu\text{g/g}$  is realistic. While this realistic value was measured on Ti-16, there is no reason to expect that Ti-7, with a higher Pd content than Ti-16, will possess a value of  $H_C$  lower than 1000  $\mu\text{g/g}$ .

The value of  $H_C$  is the hydrogen concentration above which slow crack growth is no longer observed in these tests and only fast crack growth occurs. It is sensitive to the microstructure and texture of the material with respect to the orientation of the crack and the applied stress. The hydride precipitation in the  $\alpha$ -phase, which for  $H_A > H_C$  can lead to the decrease in fracture toughness, is favored close to the basal planes (Clarke et al 1997, p. 1550). For Ti-12,  $\beta$ -phase laminations are introduced into the material through the manufacturing process (rolling) leading to a preferential pathway for cracking along these laminations. These can be easily seen in the metallographic cross sections presented in Clarke et al. (1994). Thus, the measured value of  $H_C$  for cracks propagating along these laminations is  $\sim 400$  to  $600 \mu\text{g/g}$  compared to a measured value of  $\geq 1800 \mu\text{g/g}$  for cracks propagating perpendicular to them (compare Figures 10 and 12 to Figure 14 in Clarke et al. 1994). Heat treatments to remove these laminations lead to a value of  $H_C \sim 400 \mu\text{g/g}$ , irrespective of the direction of crack propagation, since a preferential direction of orientation for hydride precipitates no longer exists. The  $H_C$  values for Ti-2 varied between 400 and  $1000 \mu\text{g/g}$  depending on the crack orientation. Heat treatments associated with welding did not significantly reduce these values (Clarke et al. 1995).

Measurements with the Pd-containing alloy Ti-16, a material with very similar properties to Ti-7, show that the value of  $H_C$  is between 1000 and  $2000 \mu\text{g/g}$  (Ikeda et al. 2000; Ikeda and Quinn 1998a, 1998b). This is thought to be due to the increased solubility of hydrogen in this material (Ikeda et al. 2000; Ikeda and Quinn 1998b). Since no  $\beta$ -phase laminations are present in Ti-16, its hydrogen-cracking behavior is not expected to be directional in the manner shown for Ti-12. Since Ti-7 possesses similar mechanical properties to Ti-16, the adoption of a model value of  $H_C$  of  $1000 \mu\text{g/g}$  is reasonable. This similarity in properties is illustrated by the equal minimum yield and ultimate tensile strengths for Ti-2, Ti-16 and Ti-7 (Been and Grauman 2000; Schutz 1995).

The values of  $H_C$  adopted in the model are conservative for other reasons also. Slow cracking in the  $\alpha$ -alloy Ti-2 is dominated by creep and plastic deformation at the crack tip leading to blunting (Clarke et al. 1997); i.e., there is no sustained load cracking as could be the case for the stronger Ti-12 (Clarke et al. 1994). This inability to achieve a sufficient stress intensity factor for fast fracture is most evident at low strain rates indicating that crack blunting should dominate under the very slow straining conditions expected under Yucca Mountain conditions. The value of  $H_C$  has also been shown to increase markedly with temperature. At  $90^\circ\text{C}$  the value of  $H_C$  for Ti-2 has been measured to be  $> 1000 \mu\text{g/g}$  (Clarke et al. 1995). Whether or not sustained load cracking or creep/plastic deformation will occur in a slow strain rate tests prior to fast fracture depends on the strength of the alloy. Since both Ti-16 and Ti-7 are  $\alpha$ -alloys with very similar strengths (minimum yield strengths are all around 275 MPa (Been and Grauman 2000)), they would be expected to exhibit similar cracking behavior. By contrast Ti-12 has a minimum yield strength of 345 MPa. To date, a critical hydrogen concentration has not been measured for Ti Grade-24, proposed for use in the support structure for the drip shield. This alloy is a much stronger material than the Ti-7 (minimum yield strength of 828 MPa [Schutz 1995]) and would be expected to experience sustained load cracking at lower hydrogen concentrations. A value of  $H_C$  for an alloy identical to Ti-24 except for the absence of Pd (i.e., Ti-5) has been measured to be  $\sim 200 \mu\text{g/g}$  using the identical experimental procedure to that employed for the other Ti alloys discussed above (Hardie and Ouyang 1999). If the influence of Pd addition is taken to have a similar effect on Ti-5 (to yield Ti-24) as its addition to Ti-2 (to yield Ti-16) did, then it is not unreasonable to expect that  $H_C$  for Ti-24 will be increased to  $400 \mu\text{g/g}$  or better.

## Criterion 2

*Is the database of general corrosion rates used in the model consistent with the rates published in the peer-reviewed literature?*

The rates used in the model are those based on weight loss measurements on specimens of Ti-7 exposed in the LTCTF at LLNL to exposure environments chosen to simulate those anticipated within Yucca Mountain (CRWMS M&O 2000a, Section 6.5.4). The rates fit a Weibull distribution with 50, 90, and 100 percentile values of 25, 100, and 350 nm/year, respectively, and comprise the most extensive database of general corrosion rates available. The rates were independent of solution composition, pH over the range 2.7 to 8.0, and temperature over the range 60°C to 90°C.

These corrosion rates can be validated by comparison to other published values. Mattsson and Olefjord (1990) measured rates in the range 0.5 to 4 nm/year on Ti-2 and Ti-7 in compacted clays saturated with saline solutions (95°C). Rates of 40 to 60 nm/year can be obtained from the plots of oxide film thickness as a function of time published by Kim and Oriani (1987b). These authors also found only a marginal increase in rate with increasing temperature between 25°C and 108°C (the boiling point of the brine). A similar absence of a temperature dependence (90°C to 200°C) was observed by Smailos and Koster (1987) and Smailos et al. (1986) for Ti-7 in aggressive Mg-dominated brines<sup>1</sup> over an exposure period of ~3.5 years. For this last set of results the rates were < 100 nm/year. Blackwood et al. (1988) measured rates in acidic (pH = -1 to 1) and alkaline solutions (pH = 14). Since they also measured a pH dependence over the acidic pH range, it was possible to estimate (by extrapolation to more neutral pH values) that the rates in more neutral environments should be in the range 15 to 20 nm/year for Ti-2. Since these rates were measured using a range of techniques from electrochemical (Blackwood et al. 1988) to surface analytical (Mattsson and Olefjord 1990; Kim and Oriani 1987b) to weight change (Smailos and Koster 1987; Smailos et al. 1986), they validate not only the values but also the weight change method used to determine the rates on the LTCTF specimens.

## Criterion 3

*Does a comparison of the rates of hydrogen absorption calculated by the model to the calculated fluxes of absorbed hydrogen within the alloy demonstrate that the assumption that all hydrogen absorbed remains in the alloy is conservative?*

The amount of hydrogen absorbed is determined in the model using the general corrosion rates (discussed above) multiplied by an electrochemically measured absorption efficiency taken from the published literature (Okada 1983). This value was measured for commercially pure titanium (equivalent to Ti-2) at pH in the range 3.5 to 4.5, but only a marginally higher value was obtained under the same conditions for titanium plated with the noble metal platinum (Okada 1983). This clearly indicates that the primary controlling factor is the presence of oxide films, not the noble metal content of the electrode surface. Consequently, the Pd-containing Ti-7 alloy would be expected to exhibit similar absorption efficiency. This similarity between the absorption behavior of commercially pure Ti (Ti-2) and Ti-7 is supported by the measurements

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<sup>1</sup> Q-brine (wt %) – 1.4 NaCl; 4.7 KCl; 26.8 MgCl<sub>2</sub>; 1.4 MgSO<sub>4</sub>; 65.7 H<sub>2</sub>O (pH = 4.9 at 25°C)

of Fukuzuka et al. (1980), who showed that, even under non-passive conditions (boiling HCl), the rate of hydrogen absorption by Ti-0.15%Pd (equivalent to Ti-7) was only a factor of two greater than for commercially pure Ti (Ti-2). Since surface analytical evidence exists to show that the oxide film formed on Ti-0.15%Pd (1.25% HCl at 125°C) becomes more passive (i.e., thickens more slowly) with time than that on Ti (Shimogori et al. 1982), its ability to prevent hydrogen formation and absorption will improve more with time than that of Ti. This justifies the adoption of a hydrogen absorption efficiency measured on Ti for use in the model with Ti-7.

There are published grounds to believe that the absorption efficiency used in the model is conservative. Thermally grown oxides (and oxides grown under pickling conditions) have been shown to increase the resistance to hydrogen absorption (Been and Grauman 2000; Covington 1979; Mon 2002, Attachment IV), and the hydrogen absorption observed in deaerated HCl ( $2 \leq \text{pH} \leq 4$ ; 50°C to 250°C) was exceedingly low under aerated conditions (Shimogori et al. 1985).

Calculations of the diffusive fluxes within the  $\alpha$ -modification of titanium using published values of diffusion coefficients (Phillips et al. 1974) indicate that any hydrogen absorbed should be transported into the bulk of the alloy. However, the accumulation of experimental evidence shows that the amount of hydrogen absorbed increases parabolically (i.e., the rate of absorption decreases) with time. This suggests that the hydrogen is accumulating in the surface region and not being transported deep into the alloy. This is particularly clear in the results of Kim and Oriani (1987b) for Ti-12. These results are particularly pertinent since they were measured in saturated brines over the temperature range 25°C to 108°C, conditions close to those anticipated in Yucca Mountain. Although the corrosion rate (measured as an oxide film growth rate) increased linearly with time, at a rate within the range measured in the LTCTF tests (CRWMS M&O 2000a, Section 6.5.2), the hydrogen absorption rate was parabolic and almost independent of temperature. It should be noted that the  $\beta$ -phase in Ti-12 leads to higher hydrogen absorption rates than would be expected in Ti-2 (Lunde and Nyborg 1993) and other  $\alpha$ -alloys. Westerman (1990) showed that the susceptible Ti-12 absorbed only small amounts of hydrogen over an 18-month exposure period to concentrated brines at 150°C and that absorption stopped after ~6 months.

These results show that hydrogen will accumulate in the surface of titanium alloys. This is likely to be more marked in Ti-7 than in Ti-12, since the former alloy does not contain the  $\beta$ -phase ligaments that facilitate diffusion into the alloy bulk (CRWMS M&O 2000c, Section 3.4). Accumulation of hydrogen in the surface of the alloy in this manner would mean that it was re-released as corrosion progressed. As a consequence, the hydrogen content of the alloy would increase more slowly than predicted by the model. This makes it very conservative to assume in the model that all the hydrogen absorbed due to general corrosion accumulates until the critical hydrogen concentration for a decrease in fracture toughness is achieved.

#### Criterion 4

*Are the hydrogen contents for grade-7 titanium and similar alloys predicted by the model consistent with values published in the peer-reviewed literature?*

The majority of hydrogen absorption measurements have been performed under aggressive conditions not relevant to Yucca Mountain; i.e., under acidic conditions or with a large cathodic potential applied to simulate cathodic protection conditions. For more relevant conditions (concentrated brines at 150°C), Westerman (1990) measured only marginal hydrogen absorption (10 to < 30 µg/g) by Ti-12 (an alloy more susceptible to hydrogen absorption than Ti-16 and Ti-7) over 12 to 18 months of exposure. The majority of the absorption appeared to occur in the first 6 months and then stop. These measurements were made in the presence of a radiation field ( $3 \times 10^4$  Rad/h) and it is possible that the hydrogen permeability of the oxide films was reduced. An improvement in resistance of the passive film on Ti-12, to hydrogen absorption in the presence of a radiation field, was also observed by Kim and Oriani (1987a). Under cathodic polarization conditions in NaCl (pH = 1) negligible amounts of hydrogen were absorbed into Ti-16 for applied potentials  $\leq -600$  mV (vs SCE) (Ikeda et al. 2000; Ikeda and Quinn 1998b). In the absence of galvanic coupling such negative potentials should be unattainable under Yucca Mountain conditions.

Of particular relevance are the results of Shimogori et al. (1985) who measured the amount of hydrogen absorbed in dilute HCl as a function of pH (2 to 4), temperature (50°C to 250°C) and degree of aeration (deaerated and aerated). Over an exposure period of 10 days the amount of hydrogen absorbed increased with a decrease in pH and an increase in temperature for deaerated conditions. For the most relevant condition (pH = 4) absorption was immeasurable at 50°C and only 1-2 µg/g at 250°C. For aerated conditions essentially no measurable hydrogen was absorbed irrespective of the pH or temperature over a similar exposure period. There is also experimental evidence that aeration suppresses hydrogen absorption by Ti-0.15Pd (equivalent to Ti-7) more than it does on by Ti (1% HCl, 70°C) (Fukuzuka et al. 1980). Since conditions within Yucca Mountain are expected to be oxidizing these results are consistent with the expectation that hydrogen absorption by the drip shield will be minor.

Two attempts to predict the hydrogen absorption rates of Ti nuclear waste containers have been published. The model adopted for the drip shield was used to predict the hydrogen absorption rates for Canadian waste containers (Shoesmith et al. 2000). In these calculations the very low corrosion rates expected in the compacted clay buffer environment proposed for this repository (0.4 to 3.3 nm/year) were used with a little higher hydrogen absorption efficiency than that used in the Yucca Mountain Project drip shield model. It was predicted that the critical hydrogen concentration of 500 µg/g would not be exceeded in  $< 10^6$  years. These calculations are to be compared with the current PA model prediction of 755 µg/g after  $10^4$  years. Based on cathodic polarization measurements as a function of applied potential, pH and duration of polarization (60 days), a parabolic hydrogen absorption relationship was adopted, and it was calculated that only 17 µg/g of hydrogen would be absorbed in  $10^3$  years (Tomari et al. 1999). Given that this model is based on a parabolic relationship compared to the linear relationship used in the current PA model, it strongly supports the model prediction that critical hydrogen concentrations will not be exceeded in  $< 10^4$  years.

**Conclusion:** In light of the above discussion, it may be concluded that the input parameter values used in the HIC model of titanium during passive general corrosion, and the model output corroborate extremely well with those reported mostly in the peer-reviewed scientific literature. It is also clear from the above discussion that the validation activities performed for building confidence in the model have sufficiently strong scientific bases, and that all of the four criteria, used to determine that the required level of confidence in the model has been achieved, have been met. Recent publication of this model in a peer-reviewed scientific journal (Shoesmith et al. 2000) has further increased the level of confidence in this model.

## **7.2 VALIDATION OF THE MODEL FOR HYDROGEN ABSORPTION BY TITANIUM UNDER GALVANICALLY COUPLED CONDITIONS**

According to the TWP (BSC 2002), model validation for HIC of titanium under galvanically coupled conditions is to be accomplished by meeting the selected criteria described below:

### **Criterion 1**

*Is the critical hydrogen concentration ( $H_C$ ) of the Grade-7 Titanium alloy (Ti-7) used by the model consistent with the results of mechanical tests published in the peer-reviewed literature?*

The critical hydrogen concentration used in this model is the same as that used in the general passive corrosion model for HIC. Since the difference between that model and this one for HIC under galvanically-coupled conditions is in the processes leading to hydrogen absorption, not in the materials properties defining the resistance to cracking, the use of an identical value of  $H_C$  is appropriate. Consequently, the arguments used to validate the values of  $H_C$  used in the general passive corrosion model are equally applicable to this model.

It should be recalled that the value of  $H_C$  used is the minimum absorbed hydrogen concentration for which a reduction in fracture toughness is observable. For general passive corrosion this concentration would be achieved universally throughout the drip shield making it vulnerable to fracture over a wide area. By contrast, in the case of galvanic coupling, hydrogen absorption will be confined to a relatively small area of the shield (~1000 to 2000 cm<sup>2</sup> affected area for the Fe/Ti contact area of ~75 cm<sup>2</sup> assumed [see Assumption 5.6] in the model). Hence, fracture would be expected to occur over a much smaller area of the shield, making the consequences of failure in the galvanically coupled case much less severe.

### **Criterion 2**

*Is the database of general corrosion rates used in the model consistent with the rates published in the peer-reviewed literature?*

In the galvanically coupled case, the rate of hydrogen absorption by the Ti-7 is the key rate used in the model. This absorption rate is supported by the corrosion rate of the coupled steel. The value used for the rate of hydrogen absorption is taken from the measurements of Murai et al (1977) (discussed in Shoesmith et al. (1995). A rate of 0.5 µg/g/day was used. This value was measured in artificial seawater (30°C) at a potential of -800 mV (vs. SCE). This is an appropriate value since the corrosion potential of a galvanic couple between carbon steel and Ti

in neutral seawater has been measured to be in the ranges -662mV to -766mV at 18°C and -736mV to -763mV at 60°C (Hodgkeiss et al. 1987).

This value of absorption rate is conservative for a number of reasons. The rate is calculated from the total amount of hydrogen absorbed over the 180-day exposure time employed and, hence, is an average linear rate over that period. A simple linear extrapolation of this rate indicates that the galvanic couple would have to persist, without any decrease in rate, for 2000 days to achieve the critical  $H_C$  value of 1000  $\mu\text{g/g}$ . Actually, since the model allows a considerable amount of hydrogen to diffuse laterally within the shield (i.e., to adjacent sites not in galvanic contact with the steel), the period required to exceed  $H_C$  would be greater. However, considerable published evidence exists to show that the rate of hydrogen absorption under galvanically coupled conditions decreases parabolically with time (Phillips et al. 1974; Noel et al. 1996; Tomari et al. 1999). This is equivalent to a decrease in the hydrogen absorption efficiency since the carbon steel corrosion rate and, hence, the rate of hydrogen production would not necessarily also decrease with time. This parabolic decrease means the actual absorption rate beyond 180 days used by Murai et al. (1977) (i.e., for the large majority of the exposure period required to exceed the  $H_C$  at the rate used in the model) would be less than the rate used in the model which assumes the constant value measured by Murai et al. (1977) applies well beyond the 180 day period over which it was measured. As a consequence the amount of hydrogen absorbed for the assumed amount of carbon steel corroded over the duration of the galvanic couple will be less than calculated by the model.

Hodgkeiss et al. (1987) have measured the current flowing in a carbon steel/Ti galvanic couple with a 1:1 contact area ( $1\text{ cm}^2$ ) in seawater (pH = 8.1; 60°C; 36–45 days exposure) to be in the range 14 to 22  $\mu\text{A}$ . The results of Mon (2002) show that the steel corrosion rate in a galvanic couple is approximately proportional to the contact area. If this proportionality is accepted and the current measured by Hodgkeiss et al. (1987) is taken to be representative of that anticipated under repository conditions, then for the assumed contact area in the model ( $\sim 75\text{ cm}^2$ ), the galvanic current would be 1,650  $\mu\text{A}$ . Application of Faradays Law then demonstrates that such a current would not produce, by a large margin, sufficient hydrogen to maintain an absorption rate of 0.5  $\mu\text{g/g/day}$  at a fractional absorption efficiency of 0.015, the value used in the model.

The key point in this conservative argument is the applicability of the data of Hodgkeiss et al. (1987) to repository conditions. Higher temperatures and more aggressive exposure environments, especially those containing  $\text{Fe}^{\text{II}}$  corrosion products (Mon 2002, Attachments I & IV), could lead to the production of considerably larger amounts of hydrogen and, hence, to higher absorption rates. However, such rates would be prevented by the production of  $\text{Fe}^{\text{III}}$  species, under oxidizing repository conditions, which are known to re-enforce the passivation of titanium (Schutz and Thomas 1987; Covington and Schutz 1981) and/or the presence of thermal oxides grown during the ventilation period or while temperatures are high prior to the formation of aqueous conditions. Substantial published evidence exists to show that thicker oxide films grown thermally (Mon 2002, Attachment III) or in a pickling solution (Mon 2002, Attachment IV), prevent hydrogen absorption up to temperatures approaching 120°C. The results reported in Mon (2002, Attachment III) show that a 40-nm thick thermally grown oxide maintains its thickness and prevents hydrogen absorption even in 2% HCl at 70°C.

### Criterion 3

*Does the comparison of the rates of hydrogen absorption calculated by the model to the calculated fluxes of absorbed hydrogen within the alloy demonstrate that the assumption all hydrogen absorbed remains in the alloy is conservative?*

Unlike the case for general passive corrosion the titanium drip shield wall is not being thinned by material loss during the galvanically coupled corrosion process. In this latter case the titanium maintains its wall thickness while cathodically absorbing hydrogen coupled to anodically corroding carbon steel. Thus, the assumption that all absorbed hydrogen remains in the alloy is realistic, not conservative.

### Criterion 4

*Are the hydrogen contents for Grade-7 titanium and similar alloys predicted by the model consistent with values published in the peer-reviewed literature?*

The majority of hydrogen absorption measurements under galvanically coupled conditions (or in the presence of cathodic polarization to simulate such conditions) have been made in aggressive environments not relevant to Yucca Mountain, i.e., in acidic environments or with a large potential that simulates cathodic protection conditions.

By comparison to the hydrogen absorption rates measured by Tomari et al. (1999) (neutral carbonate solutions of pH 8 containing 1000 µg/g of chloride at 25°C) at -750 mV (vs. SCE), the absorption rate used in the model is very conservative. Based on the parabolic relationships measured by Tomari et al. (1999), only a few tens of µg/g of hydrogen would be absorbed by Ti-2 (or Ti-17; Ti-16 with a little extra oxygen content) over thousands of years. By contrast, the rate used in the model would predict that the critical hydrogen concentration would be exceeded in ~5 to 10 years, providing support by the galvanic couple is maintained. The model rates are also conservative compared to those measured by Lee et al. (1986) in seawater (pH = 8, 25°C) which are approximately one order of magnitude lower.

A number of additional features should also be noted:

1. While the rate of hydrogen absorption is higher at higher temperatures (in the absence of a thermally grown oxide), a very large majority of the hydrogen is stored in a surface hydride layer (Noel et al. 1996; Mon 2002, Attachment II) which drastically limits the absorption rate (Noel et al. 1996). This makes the use in the model of a constant absorption efficiency of 0.015 conservative. Even for large applied potentials or applied currents (equivalent to galvanic currents well in excess of those sustainable on the drip shield [ $> 10^5$  µA through the galvanic contact area assumed in the model]) the thickness of the surface hydride layer would be only tens of microns thick. This is insufficient to threaten the full wall integrity of the drip shield.
2. Experimental evidence exists to show that the rate of hydrogen absorption (Lunde and Nyborg 1993) will decrease with the accumulation of deposits, calcite from available



CO<sub>2</sub>, and silicates from groundwater. The accumulation of silicate deposits has been well characterized in LTCTF specimens.

**Conclusion:** In light of the above discussion, it may be concluded that the input parameter values used in the HIC model of titanium under galvanically coupled condition and the model output corroborate extremely well with those reported mostly in the peer-reviewed scientific literature. It is also clear from the above discussion that the validation activities performed for building confidence in the model have sufficiently strong scientific bases and that all of the four criteria used to determine that the required level of confidence in the model has been achieved, have been met.

## 8. CONCLUSIONS

A simple and conservative model has been developed to evaluate the effects of hydrogen induced cracking on the drip shield. The basic premise of the model is that failure will occur once the hydrogen content exceeds a certain limit or critical value,  $H_C$ . Quantitative evaluation based on the HIC model described in Section 6.1 indicates that the drip shield material (Ti-7) is able to sustain the effects of HIC.

The quantitative evaluation includes analytical estimates presented in Section 6.2.3 based on Equation 2 indicating that there exists a big margin of safety for the drip shield against the effects of HIC. The hydrogen concentration in the drip shield at 10,000 years after emplacement is 755  $\mu\text{g/g}$  resulting from a conservative estimate (see Table 3). The estimated hydrogen concentration is much less than the critical hydrogen concentration of 1000  $\mu\text{g/g}$  for Ti-7, a conservative value based on Section 6.1.3.

Table 3. Output of Model for Hydrogen Absorption During Passive General Corrosion of Titanium

Output Name	Output Description	DTN	Output Uncertainty		
			Sources of Uncertainty	Uncertainty Distribution (if applicable)	Characteristic Values (if applicable)
H <sub>A</sub>	Hydrogen content in the drip shield (estimated)	N/A	Uncertainties associated with $R_{uc}$ and $f_h$	N/A	755 $\mu\text{g/g}$ (conservative value)

It may be noted that the model predictions shown in Table 3 are based on a very conservative and constant upper bound value of 0.015 for  $f_h$ . However, on the basis of available literature evidence for the absorption of hydrogen by titanium, the value of  $f_h$ , the absorption efficiency would be expected to be less than this (Tomari et al. 1999, Table 1). It should be noted that this value was measured under very aggressive electrochemically polarized conditions considered unachievable under repository conditions. Consequently,  $f_h$  may be taken to have a value between 0.005 and 0.015. The adoption of this range of values means that even the maximum value for the general passive corrosion rate will not lead to failure of the drip shield by HIC in 10,000 years. Since good published evidence exists to show the hydrogen absorption rate will

have decreased substantially long before the critical hydrogen concentration could be exceeded, it is reasonable to conclude that failure of titanium drip shield by HIC will not occur.

In a drip shield design without backfill, hydrogen generation may be caused by the galvanic coupling between the titanium drip shield surface and the ground support (such as rock bolts, wire mesh, and steel liners used in the drift), which may fall onto the drip shield surface. A qualitative assessment of HIC due to effects of galvanic coupling, as presented in Section 6.3.2, concludes that, given the high critical hydrogen concentration, the large volume of available titanium in the drip shield into which absorbed hydrogen can diffuse, and other reasons stated in Section 6.3, hydrogen embrittlement of the Ti drip shield is highly unlikely.

A parametric study based on a proposed mathematical model (Section 6.3.3) indicates that hydrogen concentration in the drip shield due to a galvanic couple will most likely not exceed the critical value. Consideration of the worst case scenario leads to the conclusion that hydrogen embrittlement is unlikely even though the hydrogen concentration may exceed the critical value. This is because of the fact that the stress intensity factor induced by a rock fall appears to be below the fracture toughness of titanium although that may be degraded by hydrogen absorption. Furthermore, if cracks do become through wall, they will be self-limited and eventually plugged by corrosion product (Section 6.3.7).

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## 10. ATTACHMENTS

No attachments.